Dissymmetrical U-Shaped π-Stacked Supramolecular Assemblies by Using a Dinuclear CuI Clip with Organophosphorus Ligands and Monotopic Fully π-Conjugated Ligands

Mehdi El sayed moussa, Kevin Guillois, Wenting Shen, Régis Réau, Jeanne Crassous, Christophe Lescop

Dissymmetrical U-shape π-stacked supramolecular assemblies using a dinuclear Cu^{I} clip bearing organophosphorus ligands and monotopic fully π-conjugated ligands.

Mehdi El Sayed Moussa, Kevin Guillois, Wenting Shen, Régis Réau, Jeanne Crassous* and Christophe Lescop*

Abstract: Reactions between the U-shape binuclear Cu^{I} complex **A** bearing short metal-metal distances and the cyano-capped monotopic π-conjugated ligands **1**-**5** carrying gradually bulkier polyaromatic terminal fragments lead to the formation of π-stacked supramolecular assemblies **6**-**10** respectively in 50-80 % yields. These derivatives have been characterized by multinuclear NMR spectroscopy and X-ray diffraction studies. Their solid state structures show the selective formation of U-shaped supramolecular assemblies in which two monotopic π-conjugated systems present large (**6**,**7**,**9**) or medium (**8**,**10**) intramolecular π-overlap revealing π-π interactions. These assemblies self-organize into head-to-tail π-stacked dimers that in turn self-assemble affording infinite columnar π-stacks. The nature, the extent and the complexity of the intermolecular contacts within the head-to-tail π-stacked dimer depends on the nature of the terminal polyaromatic fragment carried by the cyano-capped monotopic ligand but it does not alter the result of the self-assembling process. These results demonstrate that the dinuclear molecular clip **A** bearing short metal-metal distance allows selective supramolecular assembling processes driven by the formation of intra- and intermolecular short π-π interactions in the resulting self-assembled structures demonstrating that their shape is not only dictated by the symmetry of the building blocks. This approach opens perspectives toward the formation of extented π-stacked columns based on dissymmetrical and functionnal π-conjugated systems.

Introduction

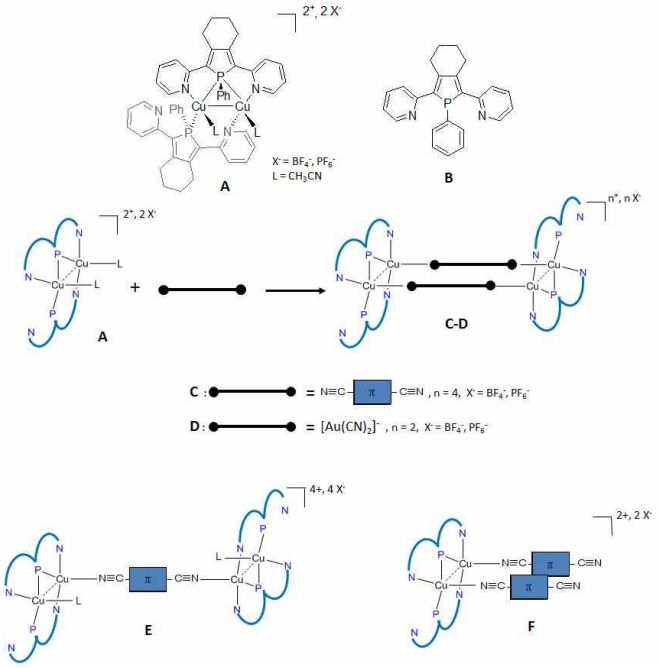
In recent years, the studies focussed on the synthesis and the physical properties of many oligomeric and polymeric π-conjugated organic systems have paved the way towards advanced materials for the development of new optoelectronic devices (light-emitting diodes, field-effect transistors, photovoltaic cells…) with enhanced physical properties, low energy consumption and ease of manufacture.[1] In this area, the solid state organization of these π-conjugated molecules and the nature and extent of intermolecular interactions they share are closely related to the photophysical properties, dimensionality, and morphology of the related material, which strongly influence the performance of the devices built from these materials.[2] Therefore the ability to control the long-range supramolecular organization of π-conjugated chromophores is a critical issue. For example, the formation of infinite π-stacked arrays is of major importance for the manufacture of efficient Organic Field Effect Transistors (OFETs) as long-range intermolecular π-overlap between the conjugated systems increases the charge-carrier mobility.[3] In order to achieve the formation of such infinite π-stacked molecular networks, non-covalent weak secondary forces such as π-π interaction,[4] hydrogen-bonding,[5] amphiphilic[6] or charge-transfer[7] interactions, and coordination bonds[8] have been utilized. However, most of these approaches require a long and sophisticated molecular engineering of the organic π-systems in a case-by-case basis which reduces the accessibility of these molecular materials, and significantly increases their cost. Therefore the development of a general and reliable synthetic approach to obtain long-range π-stacking for a large variety of π-conjugated systems is still a current subject of scientific interest.

In this field, we have previously described the coordination-driven supramolecular synthesis (also called 'directional bonding approach')[9] of a series of π-stacked supramolecular rectangles **C**[10] (Scheme 1) obtained from the reaction of homoditopic and symmetrical rigid organic π-conjugated linkers with dinuclear Cu(I) U-shape molecular clips **A**[11] based on the 2,5-bis(2-pyridyl)phosphole ligand **B**[12] (Scheme 1). This synthetic method is very versatile as demonstrated[10b] by the possibility of a large variation of the π-cores (oligo(para-phenylenevinylene)s, oligo(phenylene)s, oligo(phenylethynylene)s), but also of their length (varying from 2.7 to 22.6 Å) and of their geometry (linear, angular). Very importantly, as the π-surface of the π-conjugated linker is increased, these π-stacked supramolecular rectangles self-assemble in the solid state affording infinite columnar π-stacks.[10b] The general character of this synthetic approach was extended to the reaction of the metal-based linear linker

Dr. C. Lescop, Dr. J. Crassous, Prof. R. Réau, Dr. M. El Sayed Moussa, Dr; K. Guillois, Dr. W. Shen,
Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex (France)
Fax: (+33) 2-23-23-69-39
E-mail: christophe.lescop @univ-rennes1.fr; jeanne.crassous@univ-rennes1.fr

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

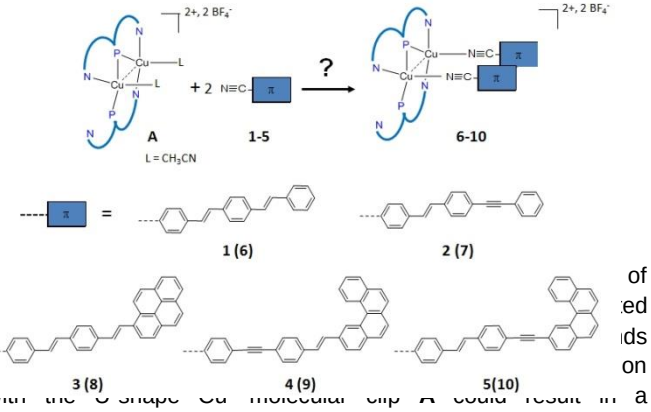
$[Au(CN)_2]^-$ with molecular clip **A**, giving rise to the 'metal rich' metallacycle **D** (Scheme 1) that displays stabilizing intramolecular and intermolecular aurophilic interactions.[13] In contrast, using $Hg(CN)_2$ which displays putative very weak mercurophilic interactions, no selective supramolecular assembly process was observed and supramolecular rectangles of type **D** were formed together with linear oligomers and 1D coordination polymers.[13] This series of results suggested that stabilizing non-covalent interlinker lateral interactions (π-π interaction, aurophilic interactions) plays a key role in the coordination driven synthetic process for driving the selective formation of metallacycles **C**, **D**. This assumption somehow does not completely support the basic concepts of coordination-driven supramolecular synthesis that rely on the consideration of the symmetry of the linking sites of the individual pre-programmed building blocks to allow a selective synthesis of a complex assembly bearing a targeted shape.



Scheme 1. Molecular structure of the derivatives **A** and **B**, Synthesis of the supramolecular metallacycles **C**-**D**, Structure of the potential intermediates **E** and **F**.

This has recently motivated us to explore the nature of the supramolecular intermediates[14] that are formed along such selective syntheses of metallacycles **C**, **D** in order to get additional insights into the driving forces governing these reactions and potentially access to new synthetic approaches affording selectively new functional molecular materials. The two supramolecular intermediates **E** and **F** (Scheme 1) were suggested on the basis of an experimental study in which the stoechiometry of the molecular clip **A** versus 'short' π-conjugated systems was varied.[14] Nevertheless, it was not possible to discriminate between these two possible intermediates **E** and **F,** which one would be responsible, if any, for the selective formation of the supramolecular metallacycles of type **C**.

These observations have triggered us to study the reaction of the U-shape molecular clip **A** with extended linear π-conjugated systems bearing *only one* terminal nitrile coordination group (Scheme 2). In these conditions, the monotopic extended linear π-conjugated systems could substitute the acetonitrile labile ligands carried by **A**, affording therefore π-stacked derivatives analog of the intermediate **F** (Scheme 1). The preparation of original and dissymmetrical π-stacked supramolecular assemblies would be thus achieved. This approach could thus give access to supramolecular assemblies bearing a variety of functions due to the possibility to use monotopic π-system bearing a large scope of terminal aromatic moieties.



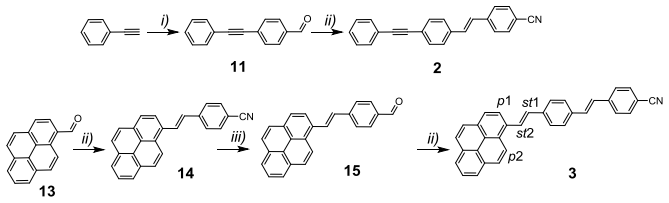
of
ed
ds
on

with the U-shape Cu molecular clip **A** could result in a substitution of the acetonitrile ligands coordinated on the Cu^I metal centers affording π-stacked dimers of type **F** (Scheme 1). The ligand **3** was subsequently designed to study whether such substitution and the self-assembly processes induced could be altered due to the presence of 'large' lateral planar polyaromatic pyrene terminal unit on the monotopic cyano-capped π-conjugated ligands reacted with **A**. Finally, the ligands **4** and **5** bearing bulkier non-planar terminal carbo[4]helicene (also called benzo[c]phenanthryl) groups were synthesized to probe the influence of the variation of the geometry and the steric congestion of the monotopic cyano-capped π-conjugated ligands on the result of their reaction with the molecular clip **A**.

Results and Discussion

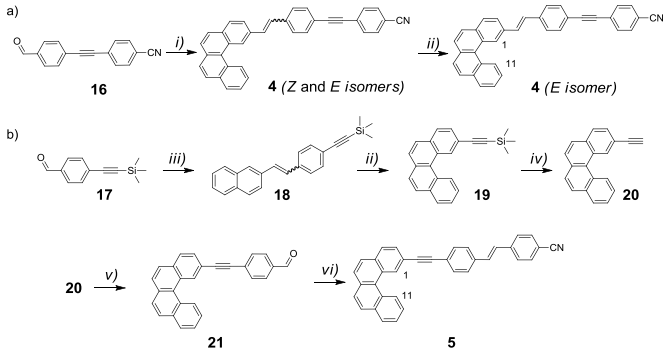
Synthesis and solid state structures of monotopic π-conjugated ligands 1-5

The synthesis of the ligand **1** was achieved according to a literature procedure.[15] The ligand **2** was obtained in two synthetic steps (Scheme 3). The first step was a Sonogashira coupling between the phenylacetylene and 4-bromobenzaldehyde to afford the derivative **11** which was subjected to a Wadsworth-Emmons reaction with the previously described diethyl(4-cyanobenzyl)phosphonate **12**[10b] leading stereoselectively to the *E*-isomer of ligand **2**. The ligand **3** was synthesized after three synthetic steps (Scheme 3). In the first step, commercially available pyrene-1-carbaldehyde was engaged in a Wadsworth-*E*mmons reaction with **12** to afford stereoselectively the *E*-isomer of derivative **14**. The nitrile group of compound **14** was reduced to an aldehyde group using DIBAL-H, giving the derivative **15**. Finally, a Wadsworth-Emmons reaction between **15** and **12** produced the targeted ligand **3** ((*E*,*E*)-isomer, Scheme 3).



Scheme 3. Synthesis of the ligands **2** and **3**. *i)* 4-bromobenzaldehyde, $PdCl_2(PPh_3)_2$, CuI, triethylamine, Ar. 50°C, one night, 80%; *ii)* diethyl(4-cyanobenzyl)phosphonate (**12**), NaH, THF, Ar, r.t., one night, 54-90%; *iii)* DIBAL-H, toluene, H_2SO_4, Ar, 30°C, 50%.

Ligand **4** was isolated after a multi-step synthesis (Scheme 4a) based on the Wittig reaction of the derivative **16**[16] and the previously described benzo[c]phenanthryl-3-yl-methyl-phosphonium bromide.[17a] A mixture of *Z* and *E* isomers was obtained and was subjected to photo-irradiation[18] with catalytic amounts of iodine exclusively affording the *E*-isomer derivative **4** (Scheme 4a). Finally, the ligand **5** was obtained after five synthetic steps (Scheme 4b). The Wittig reaction between the aldehyde derivative **17** and naphthyl-2-yl-methyl-phosphonium bromide afforded the olefin **18** as a mixture of *Z* and *E* isomers, which was then subjected to photo-irradiation[18] to produce the benzo[c]phenanthryl intermediate **19**. The TMS protecting group was removed using potassium carbonate to give the ethynyl derivative **20** that was reacted with 4-bromobenzaldehyde according to a Sonogashira coupling to produce the compound **21**. The ligand **5** was then stereoselectively obtained from the Wadsworth-Emmons reaction of **21** with the phosphonate derivative **12**.



Scheme 4. Synthesis of the ligands **4** and **5**. *i)* benzo[c]phenanthryl-3-yl-methyl-phosphonium bromide,[17] *n*-BuLi, THF, Ar, -78°C then r.t., one night, 50%; *ii)* $h\nu$, cat. I_2, toluene, one night, 80-90%; *iii)* naphthyl-2-yl-methyl-phosphonium bromide, *n*-BuLi, THF, Ar, -78°C then r.t., one night, 90%; *iv)* CH_2Cl_2/MeOH, K_2CO_3, Ar, 30°C, one night, 95%; *v)* 4-bromobenzaldehyde, $PdCl_2(PPh_3)_2$, CuI, triethylamine, Ar, 50°C, one night, 60%; *vi)* **12**, NaH, THF, Ar, r.t., one night, 86%.

Ligands **1**-**5** were isolated as air stable white (**1**, **2**), orange (**3**) or yellow (**4**, **5**) powders having good (**1**, **2**) to moderate (**3**-**5**) solubility in classical organic solvents. These derivatives have been characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Of particular interest are the ^{1}H NMR chemical shifts of the H_1 and H_{11} protons (Scheme 4) of the carbo[4]helicene derivatives all along the syntheses, which are indicative of the formation of the ortho-fused polyaromatic fragment (for example, a singlet at 9.35 ppm and a doublet at 9.17 ppm, respectively, for compound **5**). Ligands **2**-**5** were also characterized by UV-Visible and fluorescence spectroscopy (see S.I.). Finally, the solid state structures of the ligands **3**-**5** (Table 1) were determined by X-ray diffraction studies (despite several crystallization attempts, extremely thin white crystalline needles unsuitable for X-ray diffraction studies were always obtained for derivatives **1**,**2**). Homogeneous batches of single crystals of derivatives **3**-**5** were obtained at r.t. from pentane diffusion into dichloromethane solutions of **3**-**5**. One asymmetrically independent molecule is present in the unit cell of derivatives **3** and **5** while three asymmetrically independent molecules and 2.5 dichloromethane solvent molecules are observed in the case of the solid state structure of the derivative **4**. In all cases, the expected molecular structures were confirmed with all C=C double bonds having a *E*-conformation.

In the case of ligand **3** (Figure 1a), the benzonitrile and the pyrene groups have a transoid orientation with regard to the central 1,4-substituted phenyl ring. A torsion angle of ca 40° is observed between the mean plane of the pyrene unit (maximum deviation from the mean plane, 0.1 Å) and the mean plane of the stilbenyl moiety (maximum deviation from the mean plane, 0.1 Å), likely to accommodate a steric repulsion between the proton H_{p1} and H_{st1}, and H_{p2} and H_{st1} (scheme 3) carried respectively by the pyrene and stilbenyl fragments.

Table 1. Crystal data and structure refinement for ligands **3**-**5** and for the assemblies **6**-**10** (after "squeeze" treatment for **4** and **6**-**10**).

	3	**4**	**5**	**6.2BF$_4$**	**7**	**8.2BF$_4$**	**9.2BF$_4$**	**10**
Molecular formula	C_{33} H_{21} N	C_{105} H_{62} Cl_0 N_3	C_{35} H_{21} N	C_{94} H_{76} B_2 Cu_2 F_8 N_6 P_2	C_{94} H_{72} Cu_2 N_6 P_2	C_{114} H_{84} B_2 Cu_2 F_8 N_6 P_2	C_{118} H_{84} B_2 Cu_2 F_8 N_6 P_2	C_{118} H_{84} Cu_2 N_6 P_2
CCDC number	1000686	1000687	1000688	899317	899320	1000689	1000690	1000691
Molecular weight	431.51	1365.58	455.53	1652.25	1474.60	1900.51	1948.55	1774.93
***a*[Å]**	5.8588(11)	36.646(5)	16.156(4)	15.200(5)	15.857(1)	15.8929(6)	15.280(2)	15.310(2)
***b*[Å]**	7.6294(12)	5.975(5)	5.750(2)	16.218(5)	16.381(1)	17.2540(8)	15.6671(18)	22.858(5)
***c*[Å]**	48.737(9)	38.071(5)	25.921(56)	21.104(7)	21.898(2)	20.9818(11)	28.830(4)	34.177(8)
***α*[°]**	90	90	90	86.006(12)	85.376(3)	74.895(2)	79.958(5)	78.610(8)
***β*[°]**	90	106.122(5)	91.404(7)	73.617(11)	70.142(3)	70.393(2)	82.010(5)	82.439(9)
***γ*[°]**	90	90	90	75.269(10)	76.364(3)	81.383(2)	77.823(4)	73.741(8)

***V*[Å^3]**	2178.5(7)	8008(7)	2407(2)	4827(3)	5199(1)	5220.4(4)	6605.3(15)	11219(4)
Z	4	4	4	2	2	2	2	4
ρ_{calcd} [Mg m^{-3}]	1.316	1.133	1.257	1.137	0.942	1.209	0.980	1.051
crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	P212121	P21/c	P21/a	P-1	P-1	P-1	P-1	P-1
T[K]	150(2)	150(2)	150(2)	100(2)	150(2)	150(2)	150(2)	150(2)
Wavelength Mo-*K*α (Å)	0.71073	0.71069	0.71069	0.71069	0.71069	0.71073	0.71073	0.71073
Crystal size [mm]	0.25 * 0.15 * 0.04	0.4 * 0.25 * 0.08	0.2 * 0.08 * 0.06	0.3 * 0.21 * 0.1	0.25 * 0.18 * 0.12	0.22 * 0.17 * 0.10	0.4 * 0.25 * 0.08	0.25 * 0.18 * 0.04
μ ($Mo_{K\alpha}$) [cm^{-1}]	0.076	0.065	0.072	0.532	0.478	0.501	0.398	0.453
***F*(000)**	904	2852	952	1704	1532	1960	2008	3688
θ limit (°)	2.51 - 26.00	0.58 - 27.61	0.79 - 27.48	1.01 - 27.40	0.99 - 27.67	1.06 - 26.38	0.72 - 26.63	0.94 - 27.56
Index ranges *hkl*	-7 ≤ *h* ≤ 7, -9 ≤ *k* ≤ 8, -63 ≤ *l* ≤ 31	-47 ≤ *h* ≤ 29, -7 ≤ *k* ≤ 4, -49 ≤ *l* ≤ 49	-20 ≤ *h* ≤ 14, -5 ≤ *k* ≤ 7, -33 ≤ *l* ≤ 32	-19 ≤ *h* ≤ 19, -20 ≤ *k* ≤ 20, -27 ≤ *l* ≤ 26	-20 ≤ *h* ≤ 17, -21 ≤ *k* ≤ 19, -28 ≤ *l* ≤ 28	-19 ≤ *h* ≤ 19, -21 ≤ *k* ≤ 21, -26 ≤ *l* ≤ 26	-19 ≤ *h* ≤ 18, -19 ≤ *k* ≤ 19, -36 ≤ *l* ≤ 36	-19 ≤ *h* ≤ 19, -29 ≤ *k* ≤ 29, -44 ≤ *l* ≤ 34
Reflections collected	8360	34278	11711	42539	94860	45115	94902	77980
Independent reflections	4891	18371	5422	21529	23443	20774	27175	49215
Reflections [*I*>2σ(*I*)]	3586	3851	1867	12646	14085	8329	15015	10735
Data/restraints/ parameters	4891 / 0 / 307	18371 / 0 / 931	5422 / 0 / 325	21529 / 0 / 1077	23443 / 0 / 937	20774 / 0 / 1208	27175 / 0 / 1241	49215 / 0 / 2295
Goodness-of-fit on F^2	1.024	0.769	0.963	0.932	1.013	0.875	0.956	0.692
Final *R* indices [*I*>2σ(*I*)]	*R*1= 0.0537 ω*R*2= 0.1053	*R*1= 0.1133 ω*R*2= 0.2616	*R*1= 0.0885 ω*R*2= 0.1899	*R*1= 0.0607 ω*R*2= 0.1573	*R*1= 0.0887 ω*R2*= 0.2488	*R*1= 0.0762 ω*R*2= 0.1936	*R*1= 0.0685 ω*R*2= 0.1871	*R*1= 0.0854 ω*R*2= 0.2104
***R* indices (all data)**	*R*1= 0.0829 ω*R*2= 0.1185	*R*1= 0.2997 ω*R*2= 0.3328	*R*1= 0.2512 ω*R*2= 0.2751	*R*1= 0.0982 ω*R*2= 0.1727	*R*1= 0.1250 ω*R*2= 0.2780	*R*1= 0.1627 ω*R*2= 0.2198	*R*1= 0.1028 ω*R*2= 0.2022	*R*1= 0.2176 ω*R*2= 0.2401
Largest diff peak and hole (e Å^{-3})	0.191 and -0.229	0.445 and -0.563	0.221 and -0.315	1.671 and -0.696	1.574 and -0.895	0.675 and -0.594	0.682 and -0.503	0.487 and -0.696

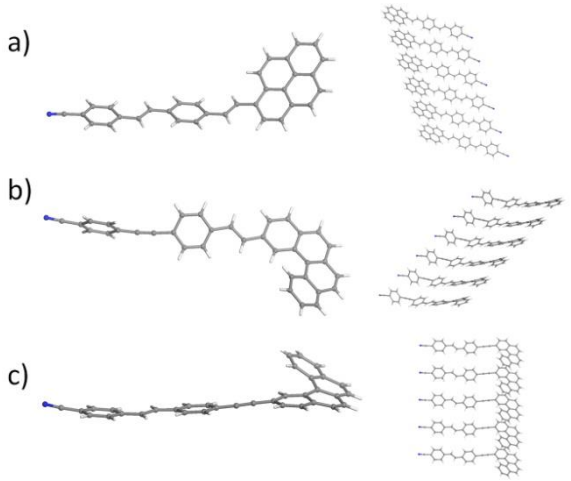


Figure 1. Views of the X-ray structure (individual molecule and the solid state packing) of: a) ligand **3**; b) ligand **4** (only the asymmetrically independent molecule bearing non-coplanar moieties is shown) and c) ligand **5**.

In the case of ligand **4**, the geometric difference between the three asymmetrically independent molecules observed is mostly related to the torsion angle of the terminal benzonitrile fragment and the central 1,4-substituted phenyl ring. In two of these molecules (Figure S2) this torsion angle is ca. 1°, while the third molecule (Figure 1b) bears a torsion angle of ca. 67°. The angle of helicity for the carbo[4]helicene fragments in the three asymmetrically independent molecules ranges between 30.6° and 32.6° which is typical for carbo[4]helicene fragments.[19] The solid state structure of the ligand **5** contains one asymmetrically independent molecule that is planar along its linear π-conjugated fragment including the first phenyl ring of the carbo[4]helicene moieties (maximum deviation from the mean plane, 0.3 Å). The angle of helicity of the carbo[4]helicene fragment in derivative **5** is ca. 31.0°.[19] Finally, note that the space groups for compounds **4**,**5** are centrosymmetric, with racemic mixtures of *P* and *M* helices of the carbo[4]helicene units. However, ligands **4**,**5** interconvert quickly in solution at r.t..[19]

In the crystal packing of derivatives **3**-**5**, columnar stacking (Figure 1) are observed with intermolecular distances (between 3.4 and 3.7 Å) revealing weak π-π interactions along these infinite columns. In the case of the ligand **4**, each of the three asymmetrically independent molecule builds up one independent π-stacked column. Note that for all ligands, intermolecular π-π contacts involve only limited fractions of neighboring pyrene (**3**) or carbo[4]helicene (**4**,**5**) fragments while the cyano-capped linear π-conjugated portions are well-isolated. These solid state structures

show that a π-π stacking involving the fully π-conjugated system of the ligands **3**-**5** is not a favoured arrangement. It is probably prohibited due to competitive effects between weak interactions and steric constraints. This results in short contacts between fractions of the large polyaromatic fragments rather than between their long linear π-conjugated moieties. Therefore a prediction of the long-range solid-state organization of these asymmetric organic π-systems considering their molecular structures is difficult, which remains a major problem in designing functional organic π-conjugated systems for material science applications.

Synthesis and solid state structures of the *U*-shape π-stacked supramolecular assemblies 6-10

The π-conjugated ligands **1**-**5** were reacted with the *U*-shape Cu^{I}-molecular clip **A** (Scheme 1) according to the following common procedure (Scheme 2): the U-shape Cu^{I}-molecular clip **A** was prepared *in situ* by the reaction in dichloromethane at r.t. of one equivalent of the ligand **B** (scheme 1) and one equivalent of $[Cu(CH_3CN)_4]BF_4$. One equivalent of the ligands **1**-**5** was added subsequently resulting in clear orange solutions that were stirred overnight at r.t.. In all cases, the $^{31}P\{^{1}H\}$ NMR spectra of the mother solutions exhibited a broad signal with a chemical shift at ca. + 8 ppm (Table 2) which is similar to those observed for the corresponding free molecular clip **A**[11] and most of the supramolecular assemblies obtained from **A** (Table S1).[10,13] These data indicate that the structure of the Cu^{I}-dimer featuring a bridging P-center is maintained along these reactions. The $^{31}P\{^{1}H\}$ NMR signals observed at r.t. are broad, mostly due to the hemilabile behaviour of ligand **B** in the coordination sphere of the Cu^{I} metal centers of the $(Cu^{I})_2(\mathbf{B})_2$ fragments.[11] $^{31}P\{^{1}H\}$ NMR signals of these crude solutions are therefore not strongly indicative of the nature of the molecular structure present in solution as both shape and chemical shift signals are mostly related to the $(Cu^{I})_2(\mathbf{B})_2$ fragment, regardless of the nature and number of the cyano-capped ligands coordinated on the metal center.[14] The crude solutions obtained were then left upon pentane vapour diffusion affording after several days homogenous polycrystalline batches of supramolecular assemblies **6**-**10** (Scheme 2) with moderate to good yields (ca. 50-80 % for crystalline batches dried overnight under reduced pressure at r.t.). $^{31}P\{^{1}H\}$ NMR spectra recorded in CD_2Cl_2 were mostly unchanged compared to those recorded for the mother solutions. ^{1}H NMR spectra in CD_2Cl_2 presented a single set of signals, with a 2:1 integration ratio between the signals assigned for the π-conjugated ligands **1**-**5** and the $(Cu^{I})_2(\mathbf{B})_2$ fragment. These signals are not significantly shifted compared to those observed for the free building blocks. Notably no signals assigned to the acetonitrile ligands was observed. These data strongly indicate a substitution of acetonitrile ligands coordinated on the Cu^{I} metal centers of the molecular clip **A** by the cyano-capped monotopic π-conjugated ligands **1**-**5** but do not allow to propose a definitive molecular structure for these species. This was finally given by single crystal X-ray diffraction studies. Single crystals of derivatives **6**-**10** were obtained at r.t. from pentane diffusion into CH_2Cl_2 solutions.

Derivatives **6** and **7** crystallize in the P-1 space group of the triclinic system (Table 1). The asymmetric unit cells of **6** and **7** contain a dicationic assembly resulting from the coordination of two ligands **1** or **2**, respectively, on a $(Cu^{I})_2(\mathbf{B})_2$ fragment (Figure 2). The asymmetric units are completed by two BF_4^- anions and, respectively, 5.5 or eight CH_2Cl_2 solvent molecules. All counter anions and cocrystallized solvent molecules are located outside the self-assembled structure. Indeed, in these derivatives, two cyano-capped monotopic π-systems have replaced the two acetonitrile ligands of **A** (Figure 2) affording 'U-shape' supramolecular assemblies. Metric data of the dicationic $(Cu^{I})_2(\mathbf{B})_2$ cores are very similar to those of the corresponding molecular clip **A** and to those generally observed for the supramolecular assemblies obtained from **A** (Tables 2 and S2).[10,11,13,14] Within the assembly **6**, one of the ligands **1** is almost fully planar (maximum deviation from the mean plane: 0.3 Å). However, the second π-ligand is not fully planar as a twist angle of ca. 27.1° is observed between the terminal phenyl ring and the remaining planar part (maximum deviation from the mean plane for the planer fragment: 0.1 Å) of this ligand. Conversely, in the derivative **7**, the two ligands **2** are almost planar (Figure 2, maximum deviation from the mean planes for both ligands **2**: 0.2 Å). In both assemblies **6** and **7**, the two π-conjugated ligands are

Table 2.

	$\delta^{31}P$, ppm	Intramolecular π-system to π-system distance (Å)	Cu-μP	Cu-N	Cu…Cu	N-Cu-μP	Cu-μP-Cu	μP-Cu-Cu	Cu-NC-	CN-Cu-Cu-NC
6	+8.6 (broad s)	3.3	2.2555(10)	2.053(3)	2.6178(11)	82.41(9)	67.32(4)	53.39(3)	2.004(3)	33.5
			2.4395(11)	2.087(3)		84.24(9)		59.29(3)	2.061(3)	
7	+8.3 (broad s)	3.4	2.2711(13)	2.039(4)	2.5924(10)	83.17(9)	67.31(4)	53.93(3)	1.986(4)	34.2
			2.4025(11)	2.042(3)		84.72(12)		58.76(3)	2.051(5)	
8	+8.1 (broad s)	3.6	2.2885(16)	2.034(5)	2.6099(9)	85.03(15)	67.76(5)	54.25(4)	2.014(6)	29.9
		2.7[b]	2.2476(17)	2.065(5)		85.16(14)		57.99(4)	2.036(5)	
9	+8.0 (broad s)	3.5	2.3156(9)	2.045(2)	2.6171(6)	84.00(8)	67.77(3)	54.99(2)	1.985(3)	35.9
			2.3777(9)	2.055(3)		84.23(8)		57.25(2)	2.080(3)	
10[a]	+8.0 (broad s)	3.3	2.2982(19)	2.024(6)	2.6127(13)	84.08(16)	67.61(6)	54.42(5)	2.050(7)	34.8
			2.396(2)	2.047(5		116.53(18)		57.98(5)	1.991(6)	
		-	-	-	-	-	-	-	-	-
		3.6	2.399(2)	2.020(5)	2.6110(13)	84.33(17)	67.70(6)	58.22(6)	2.024(7)	38.4
		2.7[b]	2.285(2)	2.070(6)		83.60(16)		54.08(5)	2.057(7)	

[a] The first series of metric data is for the conformer **10a**, the second for the conformer **10b**. [b] Intramolecular distance for the π-CH interactions

not strictly parallel to each other (angle between the main planes of the two π-systems in **6** : 16.1°; in **7**: 5.9°) and are not pointing in the same direction (Figure 2), affording a coordination angle[20] of 16.9° and 20.2°, respectively. Notably, the related coordination angle of the acetonitrile ligands in **A** (39.3°) is significantly larger than those measured in the *U*-shape π-stacked assemblies **6**,**7**. In each case, the two π–ligands are located in the vicinity of each other and short intramolecular π-π distances (ca. 3.3-3.4 Å) are observed along a large part of their backbone.

A very remarkable feature observed in the solid state structure of most of the π-stacked supramolecular metallacycles of type **C** is their self-organization within infinite π-stacked columns,[10] affording a very general approach to arrange symmetrical linear π-conjugated organic systems in infinite molecular networks in which all the π-systems overlap. Interestingly, derivatives **6** and **7** bearing dissymmetrical π-conjugated systems give also access to self-aggregated infinite π-stacked columns in the solid state. Indeed, they self-assemble into π-stacked dimers which in their turn stack into infinite colums. Each dimer of **6** or **7** (Figure 2) displays indeed a head-to-tail arrangement with short contacts involving large fractions of the π-conjugated backbone of the π-walls (intermolecular distance, ca. 3.5-3.7 Å) revealing efficient intermolecular π-π interactions (Figure 2).

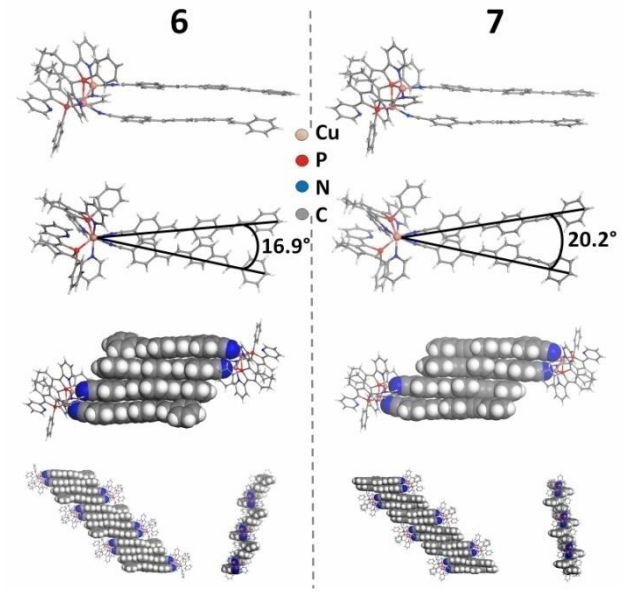


Figure 2. Side and top views of the X-ray molecular structure of tetracationic derivatives **6** and **7**; π-stacked head to tail dimers and infinite columnar π-stacks observed in the solid state structure of derivatives **6** and **7** (solvent molecules and counterions have been omitted for clarity).

These dimers of assemblies stack in their turn on each other with "interdimer π-contacts" involving a fraction of the π-surface of the neighbouring ligands **1** or **2**, respectively (Figure 2). These infinite columns are all oriented along the same direction in the bulk crystalline solid state. Finally, in these assemblies, the BF_4^- counter anions and the solvent molecules are located in columns running parallel to the π-stacked columns. The BF_4^- counter anions are mostly located in the vicinity of the $(Cu^I)_2(\mathbf{B})_2$ units. Such localization of the BF_4^- counter anions and CH_2Cl_2 solvent molecules is also observed in the other solid state structures **8**-**10**, (*vide infra*).

As a conclusion, the simple reaction of the Cu^I molecular clip **A** with the dissymmetric cyano-capped π-conjugated monotopic ligands **1** and **2** allows the preparation of new '*U*-shape' supramolecular assemblies of type **F** (Scheme 1) bearing π-stacked dimers that can subsequently self-organize within infinite π-stacked columns. Conversely to what was observed within the π-stacked supramolecular rectangles **C**,[10] in assemblies of type **F** (Scheme 1) the two π-conjugated systems are not forced to have a face to face organization along all their π-surface. Yet, π-π interactions within the self-assembled structures are still observed, as well as intermolecular π-π interactions within infinite columnar π-stacks. This result highlights the interest of using polymetallic precursors bearing such short metal-metal contacts in coordination-driven supramolecular syntheses to afford original stacked supramolecular assemblies.

These results prompted us to study the reaction of the molecular clip **A** with other linear π-conjugated systems bearing one cyano moiety as terminal coordination group. We have therefore investigated the reaction of **A** with ligand **3** (Scheme 2) bearing a pyrene moiety, affording derivative **8**. In this case, our interest was to probe the generality of such supramolecular synthetic processes towards π-stacked assemblies of dissymmetrical π-conjugated systems. Will the presence of a large planar polyaromatic group at the end of the linear monotopic π-conjugated systems alter the result of the self-assembling processes observed as the ligands **1** and **2** were reacted with **A**? X-ray single crystal analysis performed on derivative **8** revealed that it crystallizes in the P-1 space group of the triclinic system (Table 1). The asymmetric unit cell contains a dicationic assembly **8** resulting from the coordination of two ligands **3** on a $(Cu^I)_2(\mathbf{B})_2$ fragment (Figure 3a) and is completed by two BF_4^- anions and four CH_2Cl_2 solvent molecules. During the reaction, the labile acetonitrile ligands of **A** have been replaced by ligand **3**. The metric data of the dicationic $(Cu^I)_2(\mathbf{B})_2$ core in this derivative do not change significantly compared to those built-up from the molecular clip **A** (Tables 2 and S2).[10,11,13,14] Interestingly, in the solid state structure of **8**, the two ligands **3** have different geometric features. One ligand displays a torsion angle between the linear stilbenyl moiety and the pyrene fragment (ca. 42.2°) which is similar to that observed for the free ligand (ca. 40.0°, Figure 1a), while the second ligand is almost planar (maximum deviation from the mean plane of the ligand, 0.2 Å, torsion angle between the linear stilbenyl moiety and the pyrene fragment, ca. 5.6°). The coordination angle[20] (ca. 21.0°) is slightly larger than the ones observed in assemblies **6**,**7**, and the two π–ligands overlap in a parallel displaced arrangement only along a portion of the linear and almost planar stilbenyl fragments (Figure 3, intramolecular distance between the π-walls, ca. 3.6 Å, torsion angle between the mean planes of the two stilbenyl fragments, 8.7°). The two pyrene fragments are not parallel (torsion angle between the mean planes of the two planar pyrene fragments, 44.1°) and a CH-π interaction is observed between these moieties (CH-π distance ca. 2.7 Å) resulting in a cisoïd arrangement of these polyaromatic groups considering the whole symmetry of the assembly. Therefore, two cyano-capped extended π-conjugated systems bearing terminal planar polyaromatic fragments can be organized in dimers upon their coordination to the dinuclear *U*-shape molecular clip **A**, thus resulting also in assemblies of type **F** (Scheme 1). Interestingly, upon this coordination, one of the two π-systems turns out to be almost fully planar, contrary to what was observed in the free ligand **3** (Figure 1a). This fact illustrates how the coordination of organic π-conjugated systems on metal complexes can induce

structural changes on their backbone in the solid state.[21] The reason for such intramolecular organization can be explained considering the solid state organization. Indeed, similarly to compounds **6** and **7**, in the bulk crystal, assembly **8** arranges in head-to-tail manner, affording π-stacked supramolecular dimers of **8** (Figure 3). The nature of the intermolecular π-π interactions in these dimers is more complex than those observed for **6** and **7** (Figure 2). Indeed, in these dimers of assemblies **8**, the π-ligands **3** which are not planar (coloured in yellow in the Figure 3) are located close to each other with their stilbenyl moiety located mostly in the same plane. The pyrene fragments owing to these ligands are located transoïd to each other considering the symmetry of this whole aggregate (Figure 3). Above and below these π-ligands lie the ligands **3** that are almost planar. These latter ligands are involved along all their π-surface in π-π interactions (intra- and intermolecular distances, ca. 3.5 Å, Table 2) with the two 'central' non-planar π-ligands **3** owing to each of the two assemblies **8** involved in this π-stacked dimer. Therefore, in the head-to-tail dimers of **8**, the overlap of the π-systems via π-π interactions, involving the pyrene fragments, is significantly larger than if only the π-stacked dimer of ligand **3** coordinated on the $(Cu^{I})_2$(**B**)$_2$ core within the individual molecule **8** is considered (Figure 3a). In other words, the relative organisation of the ligands **3** and their conformations in the solid state structure of **8** is likely the result from a maximisation of the energy stabilisation afforded by intra- and intermolecular π-π interactions. Notably, the pending pyrene fragments (owning to the non-planar central ligands **3**) are not involved in intermolecular π-stacked interactions and probably the intramolecular CH-π interaction that is observed is a secondary stabilizing interaction that fits both with the geometric constraints lying in the core of the ligand **3** and the general organisation of the head-to-tail π-dimer of **8**. Similarly to what is observed for derivatives **6** and **7** (Figure 2), in a second stage, these head-to-tail dimers of **8** stack on top of each other to form infinite columns (Figure 3) in which all the π-systems share short π-π interactions involving a portion of the stylbenyl part of the planar ligand **3** (intermolecular distance, ca. 3.5 Å, Table 2). Notably, in these infinite columnar π-stacks, the extent of the π-π interactions is significantly larger than in the solid state structure of the free ligand **3** (Figure 1a). This confirms the ability of the $(Cu^{I})_2$(**B**)$_2$ core to force, upon coordination, a large variety of π-systems to interact via π-π interactions.[10]

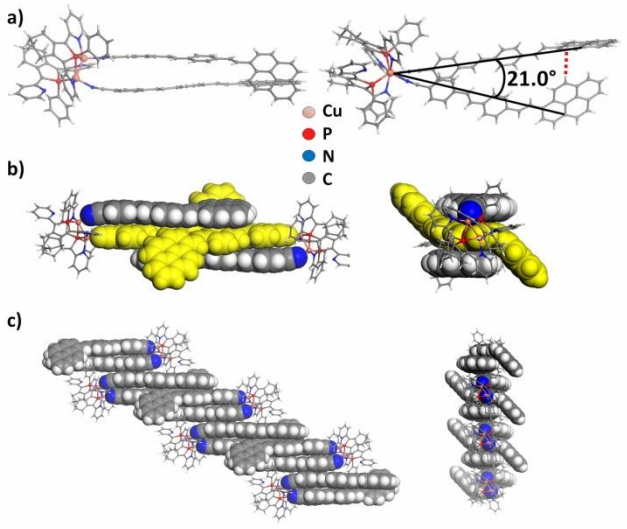


Figure 3. a) Side and top views of the X-ray molecular structure of tetracationic derivative **8** (the π-CH interaction between the two pyrene fragments is highlighted by a doted line); b) π-stacked head to tail dimers and c) infinite columnar π-stacks observed in the solid state structure of derivatives **8** (solvent molecules and counterions have been omitted for clarity).

This former example illustrates that the presence of a terminal polyaromatic pyrene moiety in the core of the cyano-capped π-conjugated ligand **3** reacted with the '*U*-shape' Cu^{I} dinuclear clip **A** does not change drastically the result of the self-assembling process observed with the ligands **1** and **2**. Notably, despite a complicated and somehow unpredictable set of inter- and/or intramolecular π-π and CH-π interactions rules out the local organisation of the molecules, a similar hierarchical self-assembling process occurs. Substitution of the acetonitrile ligands of **A** still affords new π-stacked dimers of **8** that aggregate in a head-to-tail fashion within infinite columnar π-stacks. The interest of the use of the dinuclear clip **A** in order to direct, upon coordination, the solid state supramolecular organisation of dissymmetrical π-conjugated systems is therefore confirmed.

In a next step, we have examined whether the presence of a bulkier and non planar extended π-conjugated system grafted to the cyano-capped linear π-conjugated fragment coordinated on the $(Cu^{I})_2$(**B**)$_2$ core could induce some perturbation in the self-assembling processes observed so-far. We have thus focussed our interest on ligands **4** and **5** bearing a terminal carbo[4]helicene fragment. Indeed, this ortho-fused polyaromatic group is known to be non-planar in the solid state as a result of a steric congestion between the H(1) and H(11) protons (Scheme 4) leading to an angle of helicity of ca. 30°.[19] In solution at r.t., this carbo[4]helicene is flexible and interconverts easily between the *P*-helical conformer and the *M*-helical conformer with an average planar geometry.[19] Such structural flexibility should favour the integration of carbo[4]helicene terminated monotopic non-planar π-systems within self-assembled supramolecular structures. Reaction the ligands **4** and **5** with the molecular clip **A** (scheme 2) afforded the derivatives **9** and **10**, respectively. Single crystals were obtained in good yields for these two compounds and X-ray diffraction studies (Table 1) revealed that they both crystallise in the P-1 space group of the triclinic system. The asymmetric unit cell of **9** contains a dicationic assembly resulting of the coordination of two ligands **4** on a $(Cu^{I})_2$(**B**)$_2$ fragment (Figure 4a) and is completed by two BF_4^- anions and eight CH_2Cl_2 solvent molecules. The asymmetric unit cell of **10** is more complex and contains two asymmetrically independent assemblies **10a** and **10b** (both resulting from the coordination of two ligands **5** on a $(Cu^{I})_2$(**B**)$_2$ unit, Figure 5a), four BF_4^- anions and ten CH_2Cl_2 solvent molecules. In the assembly **9**, the metric data related to the $(Cu^{I})_2$(**B**)$_2$ are not altered after the substitution of the two acetonitrile ligands of **A** by the ligands **4** (Tables 2 and S2).[10,11,13,14] Conversely to the solid state structure of the free ligand **4** (Figure 1b), a large fraction of the backbone of the two π-ligands **4** present in the assembly **9** is almost planar (maximum deviation from the mean plane including the carbon atoms of the π-conjugated system excepted those of the two final rings of the carbo[4]helicene fragment, 0.2 Å). The angle of helicity for the carbo[4]helicene fragment ranges from 25.6° to 27.3° and is smaller than those observed in the solid state structure of the free ligand **4** (30.6°-32.6°). The coordination angle[20] (7.9°, Figure 4b) is also significantly smaller than those observed in assemblies **6**-**8**. The two π-ligands are almost parallel and overlap in a face-to-face fashion along a large part of their π-walls (intramolecular π-π interaction, ca. 3.5-3.6 Å). Finally, considering the whole symmetry of the assembly **9**, the two carbo[4]helicene fragments have a cisoïd arrangement as observed in the derivative **8**.

Therefore, within the assembly **9**, the π-conjugated systems of the two ligands **4** overlap with π-π interactions along a large portion of their core. Notably, the structural diversity that was observed in the solid state structure of the ligand **4** (three conformations observed, Figure 1b) is not found in the assembly **9**, which is an illustration of how self-assembling processes can select a conformer among those possible to drive a selective synthesis. Note also that the bulk crystal is overall racemic (centrosymmetric space group), with homochiral *P*/*P*-**9** or *M*/*M*-**9** assemblies. In the bulk crystalline solid state, the derivative **9** aggregates into columns that are similar to those observed for derivatives **6** and **7** (Figure 2). These columns are based on heterochiral π-stacked dimers of **9** (Figure 4) having a head-to-tail arrangement with short contacts involving a large part of the π-surface of the π-ligands (intermolecular distance, ca. 3.5-3.6 Å, Table 2) thus revealing efficient intermolecular π-π interactions. In turn these π-stacked dimers of **9** self-assemble with fractions of their π-walls involved in π-π interaction,thus leading to the formation of infinite π-stacked columns (Figure 4).

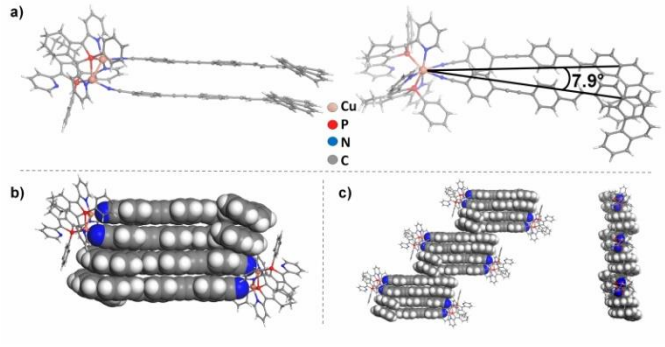


Figure 4. a) Side and top views of the X-ray molecular structure of derivative **9**; b) π-stacked head to tail dimers and c) infinite columnar π-stacks observed in the solid state structure of derivatives **9** (solvent molecules and counterions have been omitted for clarity).

The two asymmetrically independent assemblies **10a** and **10b** observed in the X-ray structure of the derivative **10** are different due to the relative orientation of the two ligands **5**. As observed in the previously described assemblies **6**-**9**, in both conformers, no significant metric changes have occured in the $(Cu^{I})_2(\mathbf{B})_2$ cores (Table 2 and table S2).[10,11,13,14] The molecular organisation observed in **10a** is quite similar of those of derivative **9** as the π-systems of the two ligands **5** are almost planar and parallel (maximum deviation from the mean planes including the carbon atoms of the π-conjugated system excepted those of the two final rings of the carbo[4]helicene fragment, 0.2 Å). The angle of helicity ranges from 26.0 to 32.2° which is comparable to that of the free ligand (31°). The coordination angle[20] in **10a** is 17.4° (Figure 5) and is larger than in the derivative **9**. In **10a**, the π-systems of the two ligands **5** overlap along a large part of their π-surfaces in a parallel displaced arrangement (Figure 5). In the asymmetrically independent molecule **10b**, the organization of the ligands **5** coordinated of the $(Cu^{I})_2(\mathbf{B})_2$ fragments is similar to those observed in the derivative **8** (Figure 3). One the two ligand **5** is almost planar in its linear part including the two first rings of the carbo[4]helicene moiety (maximum deviation from the mean plane: 0.1 Å). The angle of helicity of the carbo[4]helicene fragment of this ligand **5** is 30.9°. Conversely, the second ligand **5** coordinated on the $(Cu^{I})_2(\mathbf{B})_2$ unit is twisted twice along its π-conjugated backbone: once along the double bond (twist angle ca. 34.6°) and once along the triple bond (twist angle ca. 23.6°) of the linear fraction of this ligand. The related carbo[4]helicene moiety displays an angle of helicity of 28.4°. The coordination angle in **10b** is 22.4° (Figure 5) and the two ligands **5** in **10b** overlap with an intramolecular π-π interaction (intermolecular distance, 3.6 Å) only at the level of the phenyl ring bearing the coordinated nitrile group (Figure 5). No intramolecular π-π interactions occur further between the backbone of the two ligands **5** but an intramolecular CH-π interaction (CH-π distance ca. 2.6 Å) between the two carbo[4]helicene moieties is observed, resulting in a "T-shape orientation" of these two polyaromatic rings within the assembly **10b** (Figure 5). Note that, conversely to what was observed in the case of the derivative **9**, the two π-stacked dimers **10a** and **10b** are *P*/*M* heterochiral aggregates, an organization which certainly does not favour a good π-overlap between the π-conjugated fragments of the ligands **5** coordinated on the $Cu^{I})_2(\mathbf{B})_2$ unit. Interestingly, despite such a structural diversity in these two asymmetrically independent molecules, the bulk solid state organization of the derivative **10** also exhibits infinite columnar π-stacks. Indeed, both derivatives **10a** and **10b** form head-to tail π-stacked dimers having similar intermolecular interactions as derivatives **9** and **8**, respectively. In the case of **10a**, large overlap between the π-walls occurs with intermolecular π-π distances of ca. 3.3-3.5 Å.

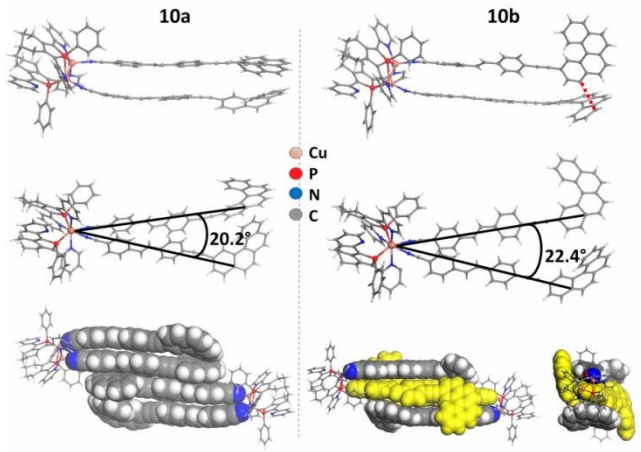


Figure 5. Side and top views of the X-ray molecular structure of the asymmetrically independent molecules **10a** and **10b** observed in the solid state structure of the derivative **10** (the π-CH interaction between the two pyrene fragments is highlighted by a doted line); π-stacked head to tail dimers observed in the solid state structure of derivatives **10a** and **10b** (solvent molecules and counterions have been omitted for clarity).

Concerning **10b** dimers, the π-systems of the four ligands **5** share π-π interactions (intermolecular distance, ca. 3.4-3.7 Å, Table 2), and two of the carbo[4]helicene moieties (owning to the π-systems located in the inner part of the head-to-tail dimer, highlighted in yellow in Figure 5) are located outside the π-stacked aggregate but connected with it due to intramolecular CH-π interaction, as in the case of the pyrene moieties in derivative **8**. Remarkably, these head-to-tail dimers of **10a** and **10b** aggregate on each other with significant π-overlapping (intermolecular distance range between 3.3 and 3.6 Å) yielding

infinite π-stacked columns alternating dimers of **10a** (blue, Figure 6) and of **10b** (green, Figure 6).

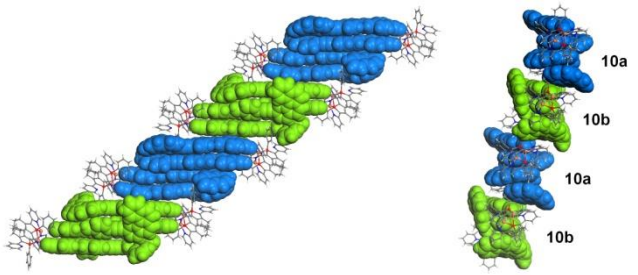


Figure 6. View of the infinite columnar π-stacked column observed in the solid state structure of the derivative **10**, highlighting the alternation of π-stacked dimers of **10a** and π-stacked dimers of **10b**.

Hence, the reaction of monotopic cyano-capped extended π-conjugated ligands **4**,**5** bearing large terminal non-planar carbo[4]helicene moieties with the molecular clip **A** still afford a hierachical self-assembly process that allow the formation of π-stacked head-to-tail dimers that in turn aggregate in infinite columnar π-stacks. Notably, as observed for derivative **8** bearing a pyrene unit, the local organization of the π-systems in **10** is quite unpredictable, probably as a result of a competition between π-π interactions, CH-π interactions and steric congestion. In addition, it is difficult to rationalize why the monotopic ligand **4** bearing a triple bond / double bond alternation and the ligand **5** bearing a double bond / triple bond alternation afford supramolecular π-stacked aggregates having such local structural differences in their organisation, with in particular the formation in the solid state of homochiral π-stacked dimers (derivative **9**, Figure 4) versus heterochiral π-stacked dimers (derivative **10**, Figure 5). Nevertheless, as long as a supramolecular π-stacked dimer is formed upon coordination of two monotopic π-systems on the $(Cu^{I})_2$(**B**)$_2$ unit, a similar aggregation of these dimers occurs affording infinite π-stacked columns in the solid state. Remarkably in these cases also, upon complexation, better π-overlap between the individual π-systems is always observed compared to those of the solid state structure of the free ligands **4** and **5**, a fact that is particularly striking in the case of the assembly **9** (Figure 4) versus the free ligand **4** (Figure 1).

Conclusion

We have shown that the reactions of the U-shape molecular clip **A** with the cyano-capped monotopic π-conjugated ligands **1**-**5** give a selective access to 'U-shape' π-stacked supramolecular assemblies **6**-**10** that form infinite columnar π-stacks in the solid state. Therefore, the very general ability of the molecular clip **A** to assemble symmetric ditopic π-conjugated systems within infinite π-stacked columns can be extended to the use of monotopic dissymmetric π-conjugated systems. These results clearly highlight how the possibility to force the π-conjugated systems to share secondary stabilizing non-covalent π-π interactions within the resulting self-assembled structures is important to drive the result of the supramolecular assembly processes based on coordination on dinuclear molecular clips bearing short intermetallic distances. Indeed, a similar hierarchical process occurs either if ditopic π-conjugated linkers (affording π-stacked supramolecular metallacycles)[10a,b] or if monotopic π-conjugated linkers (affording 'U-shape' π-stacked supramolecular assemblies) are reacted with precursor **A**. First, upon substitution of the acetonitrile ligands coordinated on the Cu^{I} metal ions of molecular clip **A**, U-shape assemblies are obtained involving strong intramolecular π-π interactions. Then, head-to-tail π-stacked dimers are formed, which in turn aggregate in the solid state into infinite π-stacked columns along which significant intermolecular π-π interactions occur. This series of results emphasizes the great potential of molecular clip **A** bearing short intermetallic distances to allow original and selective supramolecular assemblying processes.

Remarkably, the dissymmetrical cyano-capped monotopic π-conjugated systems that are involved in these self-assembly reactions can bear a large structural variety as demonstrated by the use of the derivatives **8**, **9** and **10** having terminal large planar (**8**) and non-planar (**9** and **10**) polyaromatic π-conjugated fragments. Despite the fact that the local organisation of these polyaromatic fragments is quite unpredictable, infinite columnar π-stacks are always obtained in the solid state. These series of results open therefore interesting general synthetic perpectives in order to obtain molecular materials in which electron-rich, electron-poor or larger polyaromatic fragments such as hexaperibenzocoronene or other 'nanographene' fragments bearing a cyano terminal function would be organized in infinite columnar π-stack. This class of materials is indeed of interest for the preparation of molecular materials for optoelectronic devices in which efficient charge transfer properties are requested, such as in organic solar cells or field-effect transistors.

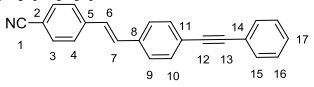
Experimental Section

General remarks

All experiments were performed under argon atmosphere using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran) or from phosphorus pentoxide (dichloromethane). Irradiations were performed using a Heraeus TQ 150 mercury vapor lamp. Preparative separations were performed by gravity column chromatography on silica gel (Merck Geduran 60, 0.063-0.200 mm) in 10-20 cm columns. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DPX200, AM300, AV400 or AV500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and were decoupled from the proton. Assignment of proton atoms is based on COSY experiment. Assignment of carbon atoms is based on HMBC, HMQC and DEPT-135 experiments. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1. UV/vis/NIR spectroscopy was conducted on a Varian Cary 5000 spectrometer.

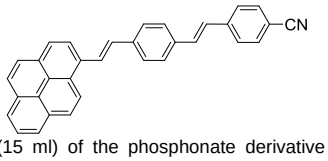
Intermediates benzo[c]phenanthrylphosphonium bromide[17], 4-[(trimethylsilyl)ethynyl]benzaldehyde **17**, [22] 4-ethynylbenzaldehyde[22] and diethyl 4-cyanobenzylphosphonate[10b] **12**, 4-((4-formylphenyl)ethynyl)benzonitrile **16**,[16] were prepared according to literature procedures. (*E*)-4-(2-(pyren-1-yl)vinyl)benzonitrile **14** was prepared according to a modified litterature procedure[23] (*E*)-4-(2-(pyren-1-yl)vinyl)benzaldehyde **15** was prepared according to a modified litterature procedure.[24]

(E)-4-(4-(phenylethynyl)styryl)benzonitrile 2



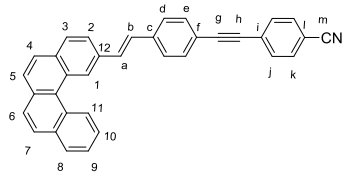
To a THF solution (40 ml) of the phosphonate derivative **12** (0.614 g, 2.42 mmol), was added five equivalents of NaH (0.290 g, 12.12 mmol). This mixture was stirred for two hours at r.t. then was added one equivalent of 4-(phenylethynyl)benzaldehyde **11** (0.500 g, 2.42 mmol). This mixture was then stirred for one night at r.t.. The crude mixture was filtered over silica, concentrated and dried under vacuum. The ligand **2** was obtained as air stable white powder (0.665 g, 2.18 mmol, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.25 (AB system, 2H, ν_{AB}= 30.9 Hz, ^3J(H,H) = 16.0 Hz, $H_{6,7}$), 7.40-7.44 (m, 3H, $H_{9,17}$), 7.58-7.60 (m, 6H, $H_{10,15,16}$), 7.69 (AB system, 4H, ν_{AB}= 12.6 Hz, ^3J(H,H) = 8.4 Hz, $H_{3,4}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 89.2 (s, C_{12}), 90.7 (s, C_{13}), 110.8 (s, C_2), 118.9 (s, C_1), 123.1 (s, C_{11}), 123.2 (s , C_{14}), 126.9 (s, C_{10}), 127.0 (s, C_4), 127.6 (s, C_6)128.4 (s, $C_{9,17}$), 131.4 (s, C_7), 131.5 (s, C_{16}), 132.0 (s , C_{15}), 132.5 (s , C_3), 136.4 (s , C_8), 141.6 (s, C_5). Mass spectrometry HR-MS (ESI): m/z found 306.1282 $[M+H]^+$; $C_{23}H_{16}N$ calcd 306.1283. Elemental analysis, calcd. (%) for $C_{23}H_{16}N$: C 90.46, H 4.95, N 4.59; found: C 90.22, H 4.68, N 4.42.

4-((E)-4-((E)-2-(pyren-1-yl)vinyl)styryl)benzonitrile 3



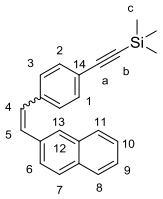
To a THF solution (15 ml) of the phosphonate derivative **12** (0.062 g, 0.24 mmol), was added five equivalents of NaH (0.024 g, 1.00 mmol). This mixture was stirred for two hours at r.t. then was added one equivalent of the aldehyde derivative **15** (0.071 g, 0.24 mmol). This mixture was then stirred for one night at r.t.. The crude mixture was filtered over silica, concentrated and purified by recrystallization (CH_2Cl_2/pentane). The ligand **3** was obtained as air stable orange powder (0.057 g, 0.13 mmol, 54%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.30 (d, ^3J(H,H) = 16.2 Hz, 1H), 7.31 (AB system, 2H, ν_{AB}= 42.4 Hz, ^3J(H,H) = 16.0 Hz), 7.69-7.63 (m, 7H), 7.75 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.03 (m, 1H), 8.09 (s, 2H), 8.19 (d, ^3J(H,H) = 9.2 Hz, 1H), 8.22 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.29 (d, ^3J(H,H) = 16.2 Hz, 1H), 8.39 (d, ^3J(H,H) = 8.0 Hz, 1H), 8.56 (d, ^3J(H,H) = 9.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 110.2 (s, C_{arom}), 120.3 (s, CN), 122.9 (s, CH_{arom}), 123.5 (s, CH_{arom}), 125.1 (s, C_{arom}), 125.4 (s, C_{arom}), 125.4 (s, C_{arom}), 125.5 (s, CH_{arom}), 125.5 (s, CH_{arom}), 125.9 (s, CH_{arom}), 126.1 (s, CH_{arom}), 126.4 (s, C_{arom}), 126.7 (s, CH_{arom}), 126.8 (s, CH_{arom}), 127.2 (s, CH_{arom}), 127.3 (s, CH_{arom}), 127.4 (s, CH_{arom}), 127.4 (s, C_{arom}), 127.7 (s, CH_{arom}), 128.4 (s, CH_{arom}), 130.9 (broad s, CH_{arom}), 131.0 (s, C_{arom}), 131.5 (s, CH_{arom}), 131.8 (s, CH_{arom}), 132.5 (s, CH_{arom}), 132.6 (s, C_{arom}), 132.6 (s, C_{arom}), 138.1 (s, C_{arom}), 141.8 (s, C_{arom}). Mass spectrometry HR-MS (ESI): m/z found 432.1743 $[M+H]^+$; $C_{33}H_{22}N$ calcd 432.1747. Elemental analysis, calcd. (%) for $C_{33}H_{22}N$: C 91.85, H 4.91, N 3.25; found: C 91.62, H 4.84, N 3.39.

(E)-4-((4-(2-(benzo[c]phenanthren-2-yl)vinyl)phenyl)ethynyl)benzonitrile 4



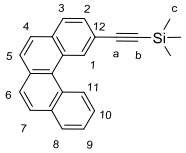
To a THF solution (40 ml) of the benzo[c]phenanthryl-3-yl-methyl-phosphonium bromide (0.583 g, 1.00 mmol), was added at -78 °C 1.2 equivalents of *n*-butyllithium (2.5N solution in hexane, 0.48 ml, 1.20 mmol). This mixture was warmed up to r.t. and was stirred for 2 hours, then was added one equivalent of derivative **15** (0.231 g, 1 mmol). This mixture was stirred for one night at r.t.. The crude mixture was then concentrated and purified by column chromatography on silica gel (AcOEt / heptane 5:95). The derivative **4** was obtained as a mixture of *E* and *Z* isomers. This mixture was then subjected to photoirradiation in toluene in the presence of a catalytic amounts of iodine. The *E* isomer of derivative **4** was obtained as air stable yellow powder (0.183 g, 0.40 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (AB system, 2H, ν_{AB}= 62.5 Hz, ^3J(H,H) = 16.3 Hz, $H_{a,b}$), 7.58 (d, 2H, ^3J(H,H) = 8.0 Hz H_d), 7.63-7.67 (m, 6H, H_e and H_i and H_k), 7.67-7.71 (m, 1H, H_9), 7.77 (ddd, 1H, *J*(H,H) = 8.4, 6.9, 1.6 Hz, H_{10}), 7.84 (d, 1H, ^3J(H,H) = 5.2 Hz, H_5), 7.87 (d, 1H, ^3J(H,H) = 5 Hz, H_4), 7.91 (d, 1H, ^3J(H,H) = 8.0 Hz, H_2), 7.95 (d, 1H, ^3J(H,H) = 8. Hz, $H_{6\ or\ 7}$), 7.99-8.03 (m, 1H, $H_{7\ or\ 6}$), 8.04 (d, 1H, ^3J(H,H) = 8.0 Hz, H_3), 8.07 (dd, 1H, *J*(H,H) = 8.0, 1.6 Hz, H_8), 9.18 (d, 1H, ^3J(H,H) = 8.5 Hz, H_{11}), 9.19 (s, 1H, H_1). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 88.7 (s, C_h), 94.1 (s, C_g), 111.5 (s, C_i), 118.5 (s, C_m), 121.2 (s, C_l), 123.2 (s, C_2), 126.0 (s, C_9), 126.3 (s, C_{10}), 126.6 (s, C_d), 126.9 (s, C_5), 127.1 (s, C_4), 127.2 (s, $C_{6\ or\ 7}$), 127.5 (s, C_1), 127.7 (s, $C_{7\ or\ 6}$), 127.8 (s, C_{11}), 128.2 (s, C_b), 128.3 (s, C), 128.7 (s , C_8), 129.0 (s, C_3), 130.3 (s, C_{arom}), 130.7 (s, C_{arom}), 130.8 (s, C_{arom}), 131.4 (s, C_{arom}), 131.8 (s, C_{arom}), 132.0 (s, C_j),132.1 (s, C_k),132.2 (s, Ce), 133.3 (s, C_{arom}), 133.6 (s, C_{arom}), 134.8 (s, C_{arom}), 138.3 (s, C_{arom}). Elemental analysis, calcd. (%) for $C_{35}H_{21}N$: C 92.28, H 4.65, N 3.07; found: C 92.42, H 4.78, N 3.32.

Trimethyl((4-(2-(naphthalen-2-yl)vinyl)phenyl)ethynyl)silane 18



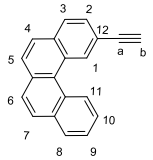
To a cold THF suspension (60 ml, -78°C) of naphthyl-2-yl-methyl-phosphonium bromide (2.000 g, 4.14 mmol), was added one equivalent of *n*-butyllithium (1.66ml, 4.14 mmol). This mixture was warmed back to r.t. and stirred for two more hours while its color turned slowly to deep red. This mixture was cooled back to -78°C and was added one equivalent of 4-[(trimethylsilyl)ethynyl]benzaldehyde **17** (0.838 g, 4.14 mmol). This mixture was warmed up to r.t. and stirred for one night, while the color turned slowly to orange - yellow. The crude mixture was filtered over silica, concentrated, and the solid was dried under vacuum. The derivative **18** was obtained as air stable white powder (1.217 g, 3.73 mmol, 90%, *Z* and *E* isomers). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.27 (s, 9H, $H_{c\ trans}$), 0.30 (s, 7H, $H_{c\ cis}$), 6.74 (AB system, 2H, ν_{AB}= 71.98 Hz, ^3J(H,H) = 12.0 Hz, $H_{4,5\ cis}$), 7.21-7.36 (m, 8H, H_{aroma} and $H_{4,5\ trans}$), 7.70-7.77 (m, 3H, H_{arom}), 7.78-7.82 (m, 1H, H_{arom}), 7.83-7.89 (m, 3H, H_{arom}). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 0.0 (s, $C_{c\ cis\ or\ trans}$), 0.1 (s, $C_{c\ cis\ or\ trans}$), 94.7 (s, C_b), 94.7 (s, C_b), 105.2 (s, C_a), 105.3 (s, C_a), 121.8 (s, C_{12}), 122.2 (s , C_{12}), 123.4 (s, CH_{arom}), 126.0 (s, CH_{arom}), 126.1 (s, CH_{arom}), 126.2 (s, CH_{arom}), 126.3 (s, CH_{arom}), 126.4 (s, CH_{arom}), 126.8 (s, CH_{arom}), 126.9 (s, CH_{arom}), 127.6 (s, CH_{arom}), 127.6 (s, CH_{arom}), 127.7 (s, CH_{arom}), 128.0 (s, CH_{arom}), 128.1 (s, CH_{arom}), 128.3 (s, CH_{arom}), 128.4 (s, CH_{arom}), 128.5 (s, C), 128.6 (s, C), 128.9 (s, CH_{arom}), 128.8 (s, CH_{arom}), 128.9 (s, CH_{arom}), 131.0 (s, CH_{arom}), 131.9 (s, CH_{arom}), 132.0 (s, C), 132.2 (s, C), 132.4 (s, CH_{arom}), 132.7 (s, C), 133.2 (s, C), 133.5 (s, C), 133.7 (s, C), 134.6 (s, CH_{arom}), 137.5 (s, C), 137.5 (s, C). ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = -17.71, -17.74. Mass spectrometry HR-MS (ESI): m/z found 327.1567 (1 ppm) $[M+H]^+$; $C_{23}H_{23}Si$ calcd 327.1569

Synthesis of intermediate (benzo[c]phenanthren-2 ylethynyl)trimethylsilane 19



To a toluene solution (750 ml) of the olefin derivative **18** (0.4 g, 1.225 mmol), was added a catalytic amount of iodine. This mixture was irradiated for one night, concentrated and purified by column chromatography on silica gel using heptane as an eluent. The derivative **19** was obtained as air stable colorless oil, which was washed several times with ethanol to remove all traces of heptane affording the product as a white solid powder (0.375 g, 1.156 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.36 (s, 9H, H_c), 7.68 (dd, 1H, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 8.3 Hz, H_2), 7.71 (ddd, 1H, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.1 Hz, H_9), 7.79 (ddd, 1H, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 8.6 Hz,^4J(H,H) = 1.5 Hz, H_{10}), 7.84 (d, 1H, ^3J(H,H) = 8.5 Hz, H_6), 7.86 (d, 1H, ^3J(H,H) = 8.4 Hz, H_5), 7.89 (d, 1H, ^3J(H,H) = 8.4 Hz, H_4), 7.94 (d, 1H, ^3J(H,H) = 8.5 Hz, H_7), 7.97 (d, 1H, ^3J(H,H) = 8.3 Hz, H_3), 8.06 (dd, 1H, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, H_8), 9.14 (d, 1H, ^3J(H,H) = 8.6 Hz, H_{11}), 9.28 (s, 1H, H_1). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 0.1 (s, C_c), 94.8 (s, C_b), 106.0 (s, C_a), 120.9 (s, C_{12}), 126.1 (s , C_9), 126.5 (s, C_{10}), 126.7 (s, C_6), 127.0 (s, C_{arom}), 127.1 (s, C_4), 127.8 (s, C_5), 127.9 (s, $C_{7,11}$), 128.5 (s, C_3), 128.6 (s, C_8), 128.8 (s, C_2), 129.9 (s , C_{arom}), 130.2 (s, C_{arom}), 131.3 (s, C_{arom}) , 131.8 (s, C_1), 133.1 (s, C_{arom}), 133.6 (s, C_{arom}). ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = -17.61. Mass spectrometry HR-MS (ESI): m/z found 325.1415 (1 ppm) $[M+H]^+$; $C_{23}H_{21}Si$ calcd 325.1412.

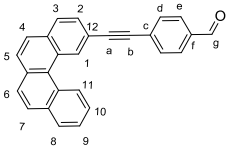
Synthesis of intermediate 2-ethynylbenzo[c]phenanthrene 20



To a 1:1 CH_2Cl_2/methanol solution (30 ml) of the silane derivative **19** (0.730 g, 2.25 mmol), was added two equivalents of K_2CO_3 (1.300 g, 4.50 mmol). This mixture was stirred for one night at 30°C, neutralized with diluted aqueous hydrochloric acid solution (1 M), and then extracted with dichloromethane (3x 20 ml). The organic phases were collected, dried over $MgSO_4$ and concentrated. The derivative **20** was obtained as air stable colorless oil, which was washed several times with ethanol to give white solid powder (0.540 g, 2.137 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 1H, H_b), 7.68 (ddd, 1H, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.2 Hz, H_9), 7.73 (d, 1H, ^3J(H,H) = 8.2 Hz, H_2), 7.77 (ddd, 1H, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.5 Hz, H_{10}), 7.84 (d, 1H, ^3J(H,H) = 8.6 Hz, H_6), 7.87 (d, 1H, ^3J(H,H) = 8.6 Hz, H_5), 7.90 (d, 1H, ^3J(H,H) = 8.6 Hz, H_4), 7.95 (d, 1H, ^3J(H,H) = 8.6 Hz, H_7), 7.99 (d, 1H, ^3J(H,H) = 8.2 Hz, H_3), 8.06 (dd, 1H, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.5 Hz, H_8), 9.11 (d, 1H, ^3J(H,H) = 8.6 Hz, H_{11}), 9.33 (s, 1H, H_1). $^{13}C\{^1H\}$ NMR (100.6 MHz,

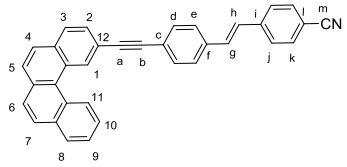
$CDCl_3$) : δ = 77.6 (s, C_b), 84.6 (s, C_a), 119.7 (s, C_{12}), 126.1 (s , C_9), 126.6 (s, C_{10}), 126.7 (s, C_6), 126.9 (s, C_{arom}), 127.0 (s, C_4), 127.7 (s, C_{11}), 128.0 (s, $C_{5,7}$), 128.6 (s, $C_{3,8}$), 128.7 (s, C_2), 129.9 (s, C_{arom}), 130.1 (s , C_{arom}), 131.3 (s, C_{arom}), 132.2 (s, C_1), 133.3 (s, C_{arom}), 133.6 (s, C_{arom}). Mass spectrometry HR-MS (ESI): m/z found 353.1010 (3 ppm) $[M+H]^+$; $C_{20}H_{13}$ calcd 353.1017.

4-(benzo[c]phenanthren-2-ylethynyl)benzaldehyde 21



4-bromobenzaldehyde (0.220 g, 0.43 mmol), the ethynyl derivative **20**, $PdCl_2(PPh_3)_2$ (0.042 g, 0.02 mmol) and CuI (0.011g, 0.02 mmol) were dried in a Schlenk tube under vacuum for 2 hours. After was added triethylamine (30 ml) under argon, and the mixture was stirred at 50°C for one night. The crude mixture was concentrated and purified by column chromatography on silica gel (AcOEt / heptane 2:98). The derivative **21** was isolated as a yellow solid (0.250 g, 0.26 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (ddd, 1H, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.2 Hz, H_9), 7.75-7.78 (m, 3H, $H_{2,d}$), 7.79 (ddd, 1H, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.4 Hz, H_{10}), 7.83 (d, 1H, ^3J(H,H) = 8.5 Hz, H_6), 7.87 (d, 1H, ^3J(H,H) = 8.6 Hz, H_5), 7.88-7.91 (m, 3H, $H_{4,e}$), 7.95 (d, 1H, ^3J(H,H) = 8.5 Hz, H_7), 8.01 (d, 1H, ^3J(H,H) = 8.2 Hz, H_3), 8.06 (dd, 1H, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.4 Hz, H_8), 9.13 (d, 1H, ^3J(H,H) = 8.6 Hz, H_{11}), 9.34 (s, 1H, H_1), 10.04 (s, 1H, H_g). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 89.2 (s, C_b), 94.5 (s, C_a), 120.1 (s, C_{12}), 126.1 (s , C_9), 126.6 (s, C_{10}), 126.7 (s, C_6), 127.0 (s, C_{arom}), 127.1 (s, C_4), 127.8 (s, C_{11}), 128.0 (s, C_7), 128.2 (s, C_5), 128.4 (s, C_2), 128.7 (s, C_8), 128.8 (s, C_3), 129.6 (s, C_e), 129.7 (s, C_{arom}), 130.0 (s, C_{arom}), 130.1 (s, C_{arom}), 131.4 (s, C_{arom}), 131.8 (s, C_1), 132.2 (s, C_d), 133.4 (s, C_{arom}), 133.6 (s, C_{arom}), 135.4 (s, C_{arom}), 191.4 (s, C_g). Mass spectrometry HR-MS (ESI): m/z found 357.1281 (0 ppm) $[M+H]^+$; $C_{27}H_{17}O$ calcd 357.1279.

Synthesis of ligand (E)-4-(4-(benzo[c]phenanthren-2-ylethynyl)styryl)benzonitrile 5



To a THF solution (60 ml) of the phosphonate derivative **12** (0.143 g, 0.56 mmol), was added five equivalents of NaH (0.070 g, 2.92 mmol). This mixture was stirred for 2 hours at r.t. then was added one equivalent of the aldehyde derivative **21** (0.200 g, 0.56 mmol). This mixture was then stirred for one night at r.t.. The crude mixture was filtered over silica, concentrated and the solid was dried under vacuum. The derivative **5** was obtained as air stable yellow powder after washing with ethanol (0.220 g, 0.48 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (AB system, 2H, ν_{AB}= 41.6 Hz, ^3J(H,H) = 16.3 Hz, $H_{g,h}$), 7.58 (d, 2H, ^3J(H,H) = 8.4 H_k), 7.61 (d, 2H, ^3J(H,H) = 8.4 H_j), 7.66-7.71 (m, 5H, $H_{9,d,e}$), 7.78 (d, 1H, ^3J(H,H) = 8.3 Hz, H_2), 7.79 (ddd, 1H, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.2 Hz, H_{10}), 7.86 (d, 1H, ^3J(H,H) = 8.5 Hz, H_6), 7.89 (d, 1H, ^3J(H,H) = 8.5 Hz, H_5), 7.92 (d, 1H, ^3J(H,H) = 8.5 Hz, H_4), 7.96 (d, 1H, ^3J(H,H) = 8.5 Hz, H_7), 8.03 (d, 1H, ^3J(H,H) = 8.3 Hz, H_3), 8.08 (d, 1H, ^3J(H,H) = 8.0 Hz, H_8), 9.17 (d, 1H, ^3J(H,H) = 8.5 Hz, H_{11}), 9.35 (s, 1H, H_1). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 89.9 (s, C_b), 92.0 (s, C_a), 110.8 (s, C_l), 119.0 (s, C_f), 120.8 (s, C_{12}), 123.5 (s, C_m), 126.1 (s , C_9), 126.6 (s, C_{10}), 126.8 (s, C_6), 126.8 (s, $C_{j\ or\ k}$), 127.0 (s, $C_{j\ or\ k}$), 127.0 (s, C), 127.1 (s, C_4), 127.5 (s, C_h), 127.8 (s, C_{11}), 127.9 (s, C_5), 128.0 (s, C_7), 128.5 (s, C_2), 128.7 (s, C_8), 128.7 (s, C_3), 130.1 (s, C_{arom}), 130.2 (s, C_{arom}), 131.4 (s, C_{arom}), 131.5 (s, C_1), 131.7 (s, C_g), 132.2 (s, $C_{d\ or\ e}$), 132.5 (s, $C_{e\ or\ d}$), 133.1 (s, C_{arom}), 133.6 (s, C_{arom}), 136.2 (s, C_{arom}), 141.6 (s, C_{arom}). Mass spectrometry HR-MS (APCI): m/z found 456.1745 (0 ppm) $[M+H]^+$; $C_{35}H_{22}N$ calcd 456.1747. Elemental analysis, calcd. (%) for $C_{35}H_{22}N$: C 92.28, H 4.65, N 3.07; found: C 92.04, H 4.88, N 3.30.

General procedure of the synthesis of supramolecular assemblies: To a dichloromethane solution (10ml) of ligand **B** (40 mg, 0.108 mmol) and $[Cu(CH_3CN)_4].BF_4$ (34mg, 0.108 mmol) was added a dichloromethane solution of ligand (1 equivalent). This reaction solution was stirred overnight and was left upon pentane vapor diffusion to afford the desired assembly as a batch of polycrystalline material. These batches of crystals were collected throught filtration over a paper of these preparations and were dried under vacuum at 40° overnight. Yields indicated correspond to the materials recovered after such crystallisations and procedure. Elemental analyses were performed on samples obtained and after these materials have been left under vacuum for one night at 40°. After this procedure, assemblies **6**-**10** were collected as red-orange powders.

Synthesis of supramolecular assembly 6: Following the general procedure, the reaction of **B** (40 mg, 0.108 mmol) and $[Cu(CH_3CN)_4].BF_4$ (34mg, 0.108 mmol) with one equivalent of **1** (0.033 g, 0.108 mmol) in 35 ml of CH_2Cl_2 afforded after crystallization **6** as an air-stable orange solid (0.005 g, 0.03 mmol, 62% yield). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.43-1.66 (m, 4H, $C=CH_2CH_2$), 1.72-1.98 (m, 4H, $C=CH_2CH_2$), 2.34-2.66 (m, 4H, $C=CH_2$), 2.88-3.14 (m, 4H, $C=CH_2$), 7.22 (AB system, 8H, ν_{AB}= 26.9 Hz, ^3J(H,H) = 16.5 Hz, $H_{6,7,12,13}$), 7.33-7.48 (m, 20H, H_5 Py, H_{Ph} and $H_{16,17}$), 7.52-7.69 (m, 24H, H_3 Py and $H_{3,4,9,10,15}$),7.94 (dd, 4H, ^3J(H,H) = 7.6Hz, H_4 Py), 8.50 (broad s, 4H, H_6 Py). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz): δ = 8.6 (broad s). Elemental analysis, calcd. (%) for $C_{94}H_{76}B_2Cu_2F_8N_6P_2.CH_2Cl_2$: C 65.68, H 4.53, N 4.84; found: C 66.10, H 4.60, N 4.36

Synthesis of supramolecular assembly 7: Following the general procedure, the reaction of **B** (40 mg, 0.108 mmol) and $[Cu(CH_3CN)_4].BF_4$ (34mg, 0.108 mmol) with one equivalent of **2** (0.035 g, 0.108 mmol) in 35 ml of CH_2Cl_2 afforded after crystallization **7** as an air-stable red solid (0.065 g, 0.0375 mmol, 75% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.20 (broad s, 4H, $C=CH_2CH_2$), 2.56 (broad s, 4H, $C=CH_2CH_2$), 3.22 (broad s, 4H, $C=CH_2$), 3.62-3.77 (m, 4H, $C=CH_2$), δ = 7.92 (AB system, 4H, ν_{AB}= 42.5 Hz, ^3J(H,H) = 16 Hz, H_6 and H_7), 8.03-8.12 (m, 20H, H_5 Py, H_{Ph} and $H_{9,17}$), 8.24-8.34 (m, 24H, H_3 Py and $H_{3,4,10,15,16}$), 8.61 (dd, 4H, ^3J(H,H) = 7.6Hz, H_4 Py), 9.16 (broad s, 4H, H_6 Py). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.98 MHz): δ = 8.3 (broad s). Elemental analysis, calcd. (%) for $C_{94}H_{76}B_2Cu_2F_8N_6P_2.2CH_2Cl_2$: C 63.42, H 4.21, N 4.62; found: C 63.50, H 4.70, N 4.85.

Synthesis of supramolecular assembly 8: Following the general procedure, the reaction of **B** (0.040 g, 0.11 mmol) and $[Cu(CH_3CN)_4].BF_4$ (0.034 g, 0.11 mmol) with one equivalent of **3** (0.043 g, 0.11 mmol) in 35 ml of CH_2Cl_2 afforded after crystallization **8** as an air-stable orange solid (0.046 g, 0.02 mmol, 46% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.45 (broad s, 4H, $C=CH_2CH_2$), 1.75 (broad s, 4H, $C=CH_2CH_2$), 2.41 (broad s, 4H, $C=CH_2$), 2.88 (broad s, 4H, $C=CH_2$), 7.09 (d, 2H, ^3J(H,H) = 16.4 Hz, H_{pyr}), 7.21 (d, 2H, ^3J(H,H) = 16.4 Hz, H_{pyr}), 7.23-7.26 (m, 14H, H_5Py and HPh), 7.32 (d, 2H, ^3J(H,H) = 16.0 Hz, H_{pyr}), 7.50-7.55 (m, 14H, H_{pyr}), 7.64 (d, 4H, ^3J(H,H) = 8.3 Hz, H_{pyr}), 7.65 (broad s, 2H, H_3Py), 7.80 (broad s, 4H, H_4Py), 7.91-8.00 (m, 6H, H_{pyr}), 8.06-8.12 (m, 6H, H_{pyr}), 8.19(d, 2H, ^3J(H,H) = 16.0 Hz, H_{pyr}), 8.26 (d, 2H, ^3J(H,H) = 8.0 Hz, H_{pyr}), 8.37 (broad s, 4H, H_6Py), 8.44 (d, 2H, ^3J(H,H) = 9.5 Hz, H_{pyr}). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 22.5 (broad s, CH_2), 28.7 (broad s, CH_2), 47.8 (broad s, CH_2), 110.2 (s, C_{arom}), 123.2 (s, CH_{arom}), 123.9 (s, CH_{arom}), 125.2 (s, C_{arom}), 125.4 (s, C_{arom}), 125.5 (s, CH_{arom}), 125.5 (s, CH_{arom}), 125.8 (s, CH_{arom}), 126.3 (s, CH_{arom}), 126.5 (s, CH_{arom}), 127.9 (s, CH_{arom}), 127.3 (s, CH_{arom}), 127.5 (s, CH_{arom}), 127.7 (s, CH_{arom}), 127.8 (s, CH_{arom}), 127.8 (s, CH_{arom}), 127.9 (s , CH_{arom}), 128.0 (s, CH_{arom}), 130.0 (broad s, CH_{arom}), 131.3 (s, C_{arom}), 131.4 (s, CH_{arom}), 131.9 (s, CH_{arom}), 132.0 (s, C_{arom}), 132.5 (s, CH_{arom}), 133.0 (s, CH_{arom}), 133.0 (s, C_{arom}), 136.3 (s, C_{arom}), 139.1 (s, C_{arom}), 139.7 (broad s, CH_{arom}), 142.7 (s, CH_{arom}), 150.4 (broad s, CH_{arom}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.98 MHz): δ = 8.13 (broad s). Elemental analysis, calcd. (%) for $C_{114}H_{84}B_2Cu_2F_8N_6P_2.CH_2Cl_2$: C 69.57, H 4.37, N 4.23; found: C 69.16, H 4.16, N 4.62.

Synthesis of supramolecular assembly 9: Following the general procedure, the reaction of **B** (0.040 g, 0.11 mmol) and $[Cu(CH_3CN)_4].BF_4$ (0.03 g, 0.11 mmol) with one equivalent of **4** (0.046 g, 0.11 mmol) in 35 ml of CH_2Cl_2 afforded after crystallization **9** as an air-stable orange solid (0.079 g, 0.02 mmol, 78% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.43 (broad s, 4H, $C=CH_2CH_2$), 1.76 (broad s, 4H, $C=CH_2CH_2$), 2.32 (broad s, 4H, $C=CH_2$), 2.84-2.89(m, 4H, $C=CH_2$), 7.12-7.33 (m, 32H), 7.41-7.61 (m, 18H), 7.74-7.88 (m, 8H), 7.93-8.02 (m, 2H), 8.35 (broad s, 4H, H_6 Py), 9.09 (d, 4H, ^3J(H,H) = 12.0 Hz, $H_{1,11}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.98 MHz): δ = 8.0 (broad s). Elemental analysis, calcd. (%) for $C_{118}H_{84}B_2Cu_2F_8N_6P_2.2CH_2Cl_2$: C 68.03, H 4.19, N 3.97; found: C 68.50, H 4.08, N 4.28.

Synthesis of supramolecular assembly 10: Following the general procedure, the reaction of **B** (0.040 g, 0.11 mmol) and $[Cu(CH_3CN)_4].BF_4$ (0.034 g, 0.11 mmol) with one equivalent of **5** (0.046 g, 0.11 mmol) in 35 ml of CH_2Cl_2 afforded after crystallization **10** as an air-stable orange solid (0.068 g, 0.02 mmol, 68% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.45 (broad s, 4H, $C=CH_2CH_2$), 1.75 (broad s, 4H, $C=CH_2CH_2$), 2.41 (broad s, 4H, $C=CH_2$), 2.81-2.98(m, 4H, $C=CH_2$), 7.04-7.27 (m, 12H, $H_{h,g,k,j}$), 7.42-7.59 (m, 24H, H_5 Py H_{Ph} and $H_{9,d,e}$), 7.65 (dd, 4H, ^3J(H,H) = 7.5 Hz, H_3 Py), 7.74-7.84 (m, 16H, H_4 Py and $H_{2,4,5,6,7,10}$), 7.88 (d, 2H, ^3J(H,H) = 8.3 Hz, H_3), 7.96 (d, 2H, ^3J(H,H) = 7.8 Hz, H_8), 8.36 (broad s, 4H, H_6 Py), 9.02 (d, 2H, ^3J(H,H) = 8.4 Hz, H_{11}), 9.21 (s, 2H, H_1). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.98 MHz): δ = 8.0 (broad s). Elemental analysis, calcd. (%) for $C_{118}H_{84}B_2Cu_2F_8N_6P_2.2CH_2Cl_2$: C 68.03, H 4.19, N 3.97; found: C 67.64, H 4.10, N 4.02.

X-ray Crystallographic Study: Single crystals suitable for X-Ray crystal analysis were obtained by slow diffusion of vapors of pentane into a dichloromethane solution of the derivatives **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10** at r.t.. Single crystal data collection were performed at 100 K or 150 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-$K\alpha$ radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization

corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[25] Structure determinations were performed by direct methods with the solving program SIR97,[26] that revealed all the non hydrogen atoms. SHELXL program[27] was used to refine the structures by full-matrix least-squares based on F^2. Most non-hydrogen atoms were refined with anisotropic displacement parameters (for more details see supplementary informations). Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. In the crystal lattices of the derivative **4**, dichloromethane solvent molecules were found in addition to the three symmetrically independent molecules found in the asymetric unit of the crystals of this monotopic cyano-capped π-conjugated. In the case of the cationic coordination complexes **6**, **7**, **8**, **9** and **10**, the tetrafluoroborate counter-anions and dichloromethane solvent molecules were found in addition in the asymetric unit of the crystals of these derivatives. In all cases these solvent molecules have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solution, a process that induce a rapid degradation of the single-crystal integrity of the crystals investigated. In order to slow down this process, single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mount at low temperature (100 K or 150 K) as quickly as possible on the diffractometer gionometer and X-ray data collection were performed at low temperature. In most of the case, X-ray crystal structure resolution revealed these solvent molecules highly disordered. In the case of the derivatives **4**, **6**, **7**, **8**, **9** and **10** disordered CH_2Cl_2 molecules occupy an important volume of the crystal cell and are found highly disorder. A correct modelling of the disorders of all these CH_2Cl_2 solvent molecules was not possible and we have proceeded to a 'squeeze' treatment in order to remove the scattering contribution of these molecules which can not be satisfactory modeled. In addition, in the case of the derivatives **7** and **10**, the tetrafluoroborate counter-anions were also found severely disorder and these tetrafluoroborate counter-anion were also involved in the 'squeeze' treatment. In the of the derivatives **3**, **5**, **7, 8** and **9**, anisotropic displacement parameters associated to the atoms of these compounds cationic coordination complexes are satisfactory. In the case of the derivative **4**, the crystals obtained were tiny plates very sensitive to rapid desolvatation of the included solvent molecules and after several attemps only, we have been able to mount a single crystal bearing a weak diffraction pattern associated with a large unit cell, that have allowed the collection of full data set. As a consequence the X-ray data collection for the derivative **4** is of poor quality and some of the atoms had to be refined with isotropic displacement parameters. In addition, in the case of the assembly **6** one part of the styryl moiety of one of the monotopic ligand **1** is disordered into two positions for which relative occupancy were refined. Some of the atoms involved in this disorder modelling have rather high anisotropic displacement parameters (origin of an ALERT A in the checkcif report). In the case of the assembly **9**, one of the fused cyclohexyl ring to the phosphole ring of one of the ligands **B** is disordered over two symetrical positions. The modelling of this disorder was not possible and consequently this ring appears planar with rather short interatomic distances for Csp3 atoms (origin of ALERTs A in the checkcif report). Also, one of the terminal carbo[4]helicene fragment bears quite high anisotropic displacement parameters for several of its carbon atoms due presumably to a disorder over several positions closely located (this disorder was not possible to be modelled). Finally in the case of the assembly **10**, single crystal collected where extremely sensitive to rapid desolvatation of the included solvent molecules and after several attemps only, we have been able to mount a single crystal bearing a weak diffraction pattern associated with a large unit cell, that have allowed the collection of full data set. As a consequence the X-ray data collection for the derivative **10** is of poor quality and some of the atoms had to be refined with isotropic displacement parameters while some other atoms associated with rather high anisotropic displacement parameters. Table 1 gives the crystallographic data for the derivatives **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10** after eventually the 'squeeze' treatment. Table S1 (see SI) gives the crystallographic data for the derivatives **4**, **6**, **7**, **8**, **9** and **10** before 'squeeze' treatment. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[28] CCDC reference numbers 1000686, 1000687, 1000688, 899317, 899320, 1000689, 1000690 and 1000691 contain the supplementary crystallographic data for derivatives **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10** respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

Acknowledgements

We thank the Ministère de la Recherche et de l'Enseignement Supérieur, the CNRS and the ANR (ANR-12-BS07-0004-METALHEL-01 and ANR-12-IS07-0002 P-OPTOELECTR-MOLMAT).

.

Keywords: supramolecular assembly • π-conjugated systems • polyaromatic fragment • π-π interaction • phosphorus ligand

[1] a) K. Müllen, G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, Weinheim, **1998**; b) L. Schmidt-Mende, A. Fechtenkotter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293,* 1119-1122; c) K. Müllen, U. Scherf, *Organic Light Emitting Devices: Synthesis, Properties and Applications,* Wiley-VCH, Weinheim, **2006**; d) S. W. Thomas, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *10,* 1339-1386; e) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107,* 1066-1096; f) S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324-1338; g) J. Roncali, P. Leriche, A. Cravino, *Adv. Mater.* **2007**, *19*, 2045-2060; h) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev*. **2009**, *109*, 5687-5754; i) Y-J. Cheng, S-H. Yang, C-S. Hsu, *Chem. Rev*. **2009**, *109*, 5868-5923; j) D.C. Bruce, D. O'Hare, R.I. Walton*, Molecular Materials*, Wiley-VCH, Chichester, **2010**, k) W. Hu, Z. Bao, K. Mullen, *J. Mater. Chem*. **2012**, *22,* 4134-4138.

[2] a) E. W. Meijer, A. P. H. J. Schenning, *Nature* **2002**, *419*, 353-354; b) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491-1546; c) A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun*. **2005**, 3245-3258; d) C-M. Chou, S-L. Lee, C-H. Chen, A. T. Biju, H-W. Wang, Y-L. Wu, G-F. Zhang, K-W. Yang, T-S. Lim, M-J. Huang, P-Y. Tsai, K-C. Lin, S-L. Huang, C-H. Chen, T-Y. Luh, *J. Am. Chem. Soc.* **2009**, 131, 12579-12585; e) B. R. Crenshaw, C. Weder, *Chem. Mater*. **2003**, *15*, 4717-4724; f) M. A. Summers, G. C. Bazan, S. K. Buratto, *J. Am. Chem. Soc.* **2005**, *127*, 16202-16206; g) R. Yang, A. Garcia, D. Korystov, A. Mikhailovsky, G. C. Bazan, T-Q. Nguyen, *J. Am. Chem. Soc.* **2006**, *128*, 16532-16539; h) R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. P. Rath, N. Tamaoki, S. J. Das, *Phys. Chem.C* **2008**, *112*, 2137-2146; i) N. S. S. Kumar, S. Varghese, N. P. Rath, S. J. Das, *Phys. Chem. C* **2008**, *112*, 8429-8437; j) J. Dong, K. M. Solntsev, L. M. Tolbert, *J. Am. Chem. Soc.* **2009**, *131*, 662-670; k) F. E. Golling, M. Quernheim, M. Wagner, T. Nishiuchi, K. Mullen, *Angew. Chem. Int. Ed.* **2014**, *53*, 1525-1528; l) D. Niedzialek, V. Lemaur, D. Dudenko, J. Shu, M.R. Hansen, J.W. Andreasen, W. Pisula, K. Mullen, J. Cornil, D. Beljonne, *Adv. Mater*, **2012**, *25*, 1939-1947.

[3] a) M-H. Yoon, A. Facchetti, C. E. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2006**, *128*, 5792-5801; b) J. S. Wu, W. Pisula, K. Müllen, *Chem. Rev*. **2007**, *107*, 718-747; c) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hagele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, *119*, 4916-4973; *Angew. Chem. Int. Ed.* **2007**, *46*, 4832-4887; d) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev*. **2007**, *36*, 1902-1929; e) X. Feng. V. Marcon, W. Pisula, M. Hansen, J. Kirkpatrick, F. Grozema, D. Andrienko, K. Kremer, K. Müllen, *Nat. Mater.* **2009**, *8*, 421-426; f) D. Wu, W. Pisula, V. Enkelmann, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2009**, *131*, 9620-9621. g) P. K. Madathil, J.-G. Lim, T.-D. Kim, D. Beckmann, A. Mavrinskiy, W. Pisula, M. Baumgarten, K. Mullen, K.-S Lee, *J. Nanosci. Nantechnol*. **2012**, *12,* 4269-4273.

[4] a) R. K. Castellano, F. Diederich, E. A. Meyer, *Angew. Chem.* **2003**, *115,* 2056-2070; *Angew. Chem. Int. Ed*. **2003**, *42*, 1210-1250; b) T. Haino, Y. Matsumoto, Y. Fukazawa, *J. Am. Chem. Soc.* **2005**, *127*, 8936-8937; c) Ž. Tomović, J. Dongen, S. J. George, H. Xu, W. Pisula, P. Leclère, M. M. J. Smulders, S. Feyter, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2007**, *129*, 16190-16196; d) K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita, *Angew. Chem.* **2007**, *119,* 1835-1838; *Angew. Chem, Int. Ed.* **2007**, *46*, 1803-1806; e) G. Fernandez, E.M. Pérez, L. Sanchez, N. Martin, *Angew. Chem.* **2008**, *120,* 1110-1113; *Angew. Chem. Int. Ed*. **2008**, *47*, 1094-1097; f) Y. Yamauchi, M. Yoshizawa, M. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 5832-5833; g) M. H. C. J. van Houtem, R. Martín-Rapún, J. A. J.M. Vekemans, E. W. Meijer, *Chem.Eur. J.* **2010**, *16,* 2258-2271; h) I. Danila, F. Riobé, F.Piron, J. Puigmartí-Luis, J. D. Wallis, M. Linares, H. Ågren, D. Beljonne, D. B. Amabilino, N. Avarvari, *J. Am. Chem. Soc*. **2011**, *133,* 8344-8353; i) P.A. Korevaar, S.J. George, A.J. Markvoort, M.M.J. Smulders, P.A.J. Hilbers, A.P.H.J. Schenning, T.F.A. de Greef, E.W. Meijer, *Nature.* **2012**, *481*, 492-496; j) W. W. H. Wong, J. Subbiah, S. R. Puniredd, B. Purushothaman, W. Pisula, N. Kirby, K. Müllen, D. J. Jones, A. B. Holmes, *J. Mater. Chem*. **2012**, *22,* 21131-21137; k) L. Chen, S. R. Puniredd,; Y.-Z. Tan, M. Baumgarten, U. Zschieschang, V. Enkelmann, W. Pisula, X. Feng, H.

Klauk, K. Müllen, *J. Am. Chem. Soc,* **2012**, *134,* 17869-17872; l) X. Guo, S. R. Puniredd, M. Baumgarten, W. Pisula, K. Müllen, *J. Am. Chem. Soc,* **2013**, *134,* 20, 8404-8407; m) P.A. Korevaar, T.F.A. de Greef, E.W. Meijer, *Chem. Mater.* **2014**, *26,* 576-586.

[5] a) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601-1604; b) J. H. K. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167-170; c) J.-H. Fournier, T. Maris, J. D. Wuest, *J. Org. Chem*. **2004**, *69*, 1762−1775; d) J. D. Wuest, *Chem. Commun*. **2005**, 5830−5837; e) N. Malek, T. Maris, M. Simard, J. D. Wuest*, J. Am. Chem. Soc*. **2005**, *127*, 5910−5916; f) K. E. Maly, E. Gagnon, T. Maris, J. D. Wuest, *J. Am. Chem. Soc*. **2007**, *129*, 4306-4322 ; g) L. R. MacGillivray, G. S. Papaefstathiou, T. Friscic, T. D. Hamilton, D.-K. Bucar, Q. Chu, D. B. Varshney, I. G. Georgiev, Acc*. Chem. Res.* **2008**, *41*, 280-291 ; h) R. Matmour, I. D. Cat, S. J. George, W. Adriaens, P. Leclère, P. H. H. Bomans, N. A. J. M. Sommerdijk, J. C. Gielen, P. C. M. Christianen, J. T. Heldens, J. C. M. Hest, D. W. P. M. Lwik, S. D. Feyter, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc*. **2008**, *130*, 14576-14583; i) R. Abbel, C. Grenier, M. J. Pouderoijen, J. W. Stouwdam, P. Leclère, R. P. Sijbesma, E. W. Meijer, A. P. H. J. Schenning*, J. Am. Chem. Soc.* **2009**, *131*, 833-843; j) T. Friscic, L. R. MacGillivray, *Chem. Commun*. **2009**, 773-775; k) A. Llanes-Pallas, C.-A. Palma, L. Piot, A. Belbakra, A. Listorti, M. Prato, P. Samor, N. Armaroli, D. Bonifazi, *J. Am. Chem. Soc*. **2009**, *131*, 509-520; l) Z. Li, F. W. Fowler, J. W. Lauher*, J. Am. Chem. Soc*. **2009**, *131*, 634-643. m) T. S.J. George, R. de Bruijn, Z. Tomovic, B. van Averbeke, D. Beljonne, R. Lazzaroni, A.P.H.J. Schenning and E.W. Meijer, *J. Am. Chem. Soc.* **2012***, 134*, 17789-17796. n) T. Mes, S. Cantekin, D.W.R. Balkenende, M.M.M. Frissen, M.A.J. Gillissen, B.F.M. de Waal, I.K. Voets, E.W. Meijer and A.R.A. Palmans, *Chem. Eur. J.* **2013***, 19*, 8642-8649.

[6] a) M. Lee, J. W. Kim, S. Peleshanko, K. Larson, Y. S. Yoo, D. Vaknin, S. Markutsya, V. V. Tsukruk, *J. Am. Chem. Soc.* **2002**, *124*, 9121-9128; b) V. Percec, M. Glodde, M. Peterca, A. Rapp, I. Schnell, H. W. Spiess, T. K. Bera, Y. Miura, V. S. K. Balagurusamy, E. Aqad, P. A. Heiney, *Chem. Eur. J,* **2006**, *12,* 6298- 6314. c) Y. Yamamoto, T. Fukushima, A. Saeki, S. Seki, S. Tagawa, N. Ishii and T. Aida, *J. Am. Chem. Soc*. **2007**, *129*, 9276-9277; d) W. S. Li, Y. Yamamoto, T. Fukushima, A. Saeki, S. Seki, S. Tagawa, H. Masunaga, S. Sasaki, M. Takata and T. Aida, *J. Am. Chem. Soc*. **2008**, *130*, 8886-8887; e) Y. Yamamoto, G. X. Zhang, W. S. Jin, T. Fukushima, N. Ishii, A. Saeki, S. Seki, S. Tagawa, T. Minari, K. Tsukagoshi and T. Aida, *Proc. Natl. Acad. Sci. U. S. A*. **2009**, *106*, 21051-21056. f) M.A.J. Gillissen, M.M.E. Koenigs, J.J.H. Spiering, J.A.J.M. Vekemans, A.R.A. Palmans, I.K. Voets, E.W. Meijer, *J. Am. Chem. Soc.* **2014***, 136*, 336-343.

[7] a) J. Herrikhuyzen, A. Syamakumari, A. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2004**, *126*, 10021-10027. b) M. Treier, A. Liscio, J. M. Mativetsky, M. Kastler, K. Müllen, V. Palermo, P. Samori, *NANOSCALE*, **2012**, *4,* 1677-1681.

[8] a) J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH: Weinheim, **1995**; b) J-P. Sauvage, *Transition metals in supramolecular chemistry*, Wiley and Sons, Chichester, **1994**; c) A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem.* **1998**, *110,* 2327-2331; *Angew. Chem. Int. Ed.* **1998**, *37*, 2205-2208; d) K. Binnemans, K. Lodewyckx, B. Donnio, D. Guillon, *Chem. Eur. J.* **2002**, *8*, 1101-1105; e) J. Barberá, R. Giménez, N. Gimeno, M. Marcos, M. D. C. Pina, J. L. Serrano, *Liq. Cryst.* **2003**, *30*, 651-661; f) L. Douce, T. H. Diep, R. Ziessel, A. Skoulios, M. Césario, *J. Mater. Chem.* **2003**, *13*, 1533-1539; g) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J. -M. Lehn, *Angew. Chem.* **2004**, *116, 3728-3747; Angew. Chem. Int. Ed. Engl*. **2004**, *43*, 3644-3662; h) J.-Q. Jiang, Z.-R. Shen, J. Lu, P.-F. Fu, Y. Lin, H.-D. Tang, H.-W. Gu, J. Sun, P. Xie, R.-B. Zhang, *Adv. Mater.* **2004**, *16*, 1534-1539; i) M. Marcos, A. Omenat, J. Barberá, F. Durán, J. L. Serrano, *J. Mater. Chem.* **2004**, *14*, 3321-3327; j) D. M. Huck, H. L. Nguyen, B. Donnio, D. W. Bruce, *Liq. Cryst.* **2004**, *31*, 503-507; k) O. Maury, H. Le Bozec, *Acc. Chem. Soc*. **2005**, *38*, 691-704; l) M C. Torralba, D. M. Huck, H. L. Nguyen, P. N. Horton, B. Donnio, M. B. Hursthouse, D. W. Bruce, *Liq. Cryst.* **2006**, *33*, 399-407; m) U. Schlickum, R. Decker, F. Klappenberger, G. Zoppellaro, S. Klyastskaya, M. Ruben, I. Silanes, A. Arnau, K. Kern, H. Brune, J. V. Barth, *Nano Lett.* **2007**, *7*, 3813-3817; n) S. Graule, M. Rudolph, N. Vanthuyne, J. Autschbach, C. Roussel, J. Crassous, R. Réau, *J. Am. Chem. Soc.* **2009**, 131, 3183-3185.

[9] a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853-908; b) R. S. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972-983; c) G. J.; Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113,* 2076-2097; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022-2043; d) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759-771; e) R. J. Puddephatt, *Coord. Chem. Rev.* **2001**, *216-217*, 313-332; f) M. Fujita, M. Tominaga, A. Aoai, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369-378; g) N.C. Gianneschi, M. S. Masar III, C. A. Mirkin, *Acc. Chem. Res.* **2005**, *38*, 825-837; h) S. J. Lee, W. Lin, *Acc. Chem. Res*. **2008**, *41*, 521; for recent reviews and articles: i) B. Therrien, *Eur. J. Inorg. Chem.* **2009**, *17*, 2445-2453; j) B. H. Northrop, Y. R. Zheng, K. W. Chi, P. J. Stang, *Acc. Chem. Res.* **2009**, *42*, 1554-1563; k) P. J. Stang, *J. Org. Chem.* **2009**, *74*, 2-20; l) M. Yoshizawa, J. Klosterman, M. Fujita, *Angew. Chem.* **2009**, *121*, 3470-3490; *Angew. Chem., Int. Ed*. **2009**, *48*, 3418-3438; m) Y.R. Zheng, P.J. Stang, *J. Am. Chem. Soc.* **2009**, *131*, 3487-3489; n) P. Jin, S. J. Dalgarno, J. L. Atwood, *Coord. Chem. Rev.* **2010**, *254*, 1760-1768; o) R. Chakrabarty, P. S. Mukherjee, P J. Stang, *Chem. Rev.* **2011**, *111*, 6810-6918; p) Y. Inokuma, M. Kawano, M. Fujita, *Nat. Chem.* **2011**, *3*, 349-358; q) H. Amouri, C. Desmarets, J. Moussa, *Chem.Rev.* **2012**, *112*, 2015-2041; r) L. R. MacGillivray, *Angew. Chem.* **2012**, *124*, 1136-1138; *Angew. Chem., Int. Ed.* **2012**, *51*, 1110-1112; s) K. Harris, Q. Sun, S. Sato, M. Fujita, *J. Am. Chem. Soc.* **2013**, *135*, 12497-12499; t) K. Harris, D. Fujita, M. Fujita, *Chem. Commun.* **2013**, *49,* 6703-6712; u) Y. Fang, T. Murase, S. Sato, M. Fujita, *J. Am. Chem. Soc.* **2013**, *135*, 613-615; v) M. Yoneya, S. Tsuzuki, T. Yamaguchi, S. Sato, M. Fujita, *ACS Nano.* **2014**, *8*, 1290-1296; w) H. Takezawa, T. Murase, G. Resnati, P. Metrangolo, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 1786−1788. x) T. Sawada, H. Hisada, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 4449-4451; y) J.-P. Ma, S.-Q. Wang, C.-W. Zhao, H.-Y. Wang, Y.-B. Dong, *Chem. Commun.* **2014**, *50*, 4721-4724; z) L. Xu, L.-J. Chen, H.-B. Yang, *Chem. Commun.* **2014**, *50*, 5156-5170.

[10] a) B. Nohra, S. Graule, C. Lescop, R. Réau, *J. Am. Chem. Soc.* **2006**, *128*, 3520-3521; b) Y. Yao, W. Shen, B. Nohra, C. Lescop, R. Réau, *Chem. Eur. J.* **2010**, *16*, 7143-7163; c) A. I. Aranda Perez, T. Biet, S. Graule, T. Agou, C. Lescop, N. R. Branda, J. Crassous, R. Réau, *Chem. Eur. J.* **2011**, *17*, 1337-1351.

[11] a) F. Leca, C. Lescop, E. Rodriguez-Sanz, K. Costuas, J-F. Halet, R. Réau, *Angew. Chem. Int. Ed.*, **2005**, *44*, 4362-4365; b) B. Nohra, E. Rodriguez-Sanz, C. Lescop, R. Réau, *Chem. Eur. J.*, **2008**, *14*, 3391-3403.

[12] a) D. Le Vilain, C. Hay, V. Deborde, L. Toupet, R. Réau, *Chem. Commun*. **1999**, 345-346; b) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi, R. Réau, *Chem. Eur. J.* **2001**, *7*, 4222-4236.

[13] V. Vreshch, W. Shen, B. Nohra, S-K Yip, V.W-W. Yam, C. Lescop, R. Réau, *Chem. Eur. J.*, **2012**, *2*, 466-477.

[14] B. Nohra, R. Réau, C. Lescop, *Eur. J. Inorg. Chem*, **2014**, *10*, 1788-1796.

[15] D. P. Flaherty, Y. Dong, J. L. Vennerstrom,*Tetrahedron Lett.*, **2009**, 50, 6228-6230.

[16] C. Richardson, C. A. Reed, *J. Org. Chem*. **2007**, *72*, 4750-4755.

[17] D.A. Lightner, D. T. Hefelfinger, T. W. Powers, G. W. Frank, K. N. Trueblood, *J. Am. Chem. Soc.* **1972**, *94*, 3492-3497.

[18] a) Y. Shen, C.-F. Chen, *Chem. Rev*. **2012**, *112*, 1463-1535; b) S. Graule, M. Rudolph, W. Shen, C. Lescop, J. A. G. Williams, J. Autschbach, J. Crassous, R. Réau, *Chem. Eur. J*. **2010,** *16,* 5976-6005; c) M. El Sayed Moussa, M. Srebro, E. Anger, N. Vanthuyne, C. Roussel, C. Lescop, J. Autschbach, J. Crassous, *Chirality*, **2013**, *25*, 455-465.

[19] The angle of helicity is defined by the torsion angle measured between the planes defined by the terminal phenyl rings. See: E. Anger, M. Rudolph, L. Norel, S. Zrig, C. Shen, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, R. Reau. *Chem. Eur. J*. **2011**, *17*, 14178-14198 and ref. 18b.

[20] The coordination angle is defined by the torsion angle "C_A-Cu_1-Cu_2-C_B" where C_A and C_B are the carbon atoms in the para position of the phenyl rings that attaches the lateral π-conjugated systems to the connecting linear π-conjugated system.

[21] H. Chen, W. Delaunay, L. Yu, D. Joly, Z. Wang, J. Li, Z. Wang, C. Lescop, D. Tondelier, B. Geffroy, Z. Duan, M. Hissler, F. Mathey, R. Réau, *Angew. Chem. Int. Ed.* **2012**, *1,* 214-217.

[22] B.W. Austin, N. Bilow, W.J. Kelleghan, K.S.Y. Lau, *J. Org. Chem.* **1981**, *46*, 2280-2286.

[23] M. Beinhoff, W. Weigel, M. Jurczok, W. Rettig, C. Modrakowski, I. Brudgam, H. Hartl, A. D. Schluter, *Eur. J. Org. Chem.* **2001***, 20,* 3819-3829.

[24] A. Cirpan, H. P. Rathnayake, P. M. Lahti, F. E. Karasz, *J. Mater. Chem.* **2007***, 17,* 3030-3036.

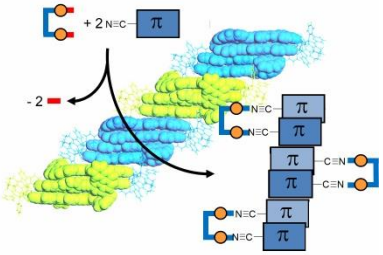
[25] Z. Otwinowski, W. In Minor, *Methods in Enzymology*, (Ed.: C.W. Carter, Jr. & R.M. Sweet)*,* New York:Academic Press, **1997**, *276*, 307.

[26] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. of Applied Cryst.* **1999***, 32,* 115.

[27] G.M. Sheldrick, *SHELX97,* Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

[28] International Tables for X-ray Crystallography, vol C, Ed. Kluwer, Dordrech, **1992**.

A general approach to π-stacked dissymmetrical supramolecular assemblies is described. Reaction of a series of dissymmetrical cyano-capped monotopic π-conjugated systems with a U-shape Cu^{I} dinuclear molecular clip results in the formation of U-shape π-stacked supramolecular assemblies that self-assemble in the solid state along infinite columns of interacting π -systems regardless to the nature of the π-conjugated system.



Subject Heading

Mehdi El Sayed Moussa, Kevin Guillois, Wenting Shen, Régis Réau, Jeanne Crassous and Christophe Lescop**

■■ - ■■

Dissymmetrical U-shape π-stacked supramolecular assemblies using a dinuclear Cu^{I} clip bearing organophosphorus ligands and monotopic fully π-conjugated ligands.